PB85-245298

Industrial Process Profiles for Environmental Use. Chapter 10a The Plastics and Resins Processing Industry

Radian Corp., McLean, VA

Prepared for

Environmental Protection Agency, Cincinnati, OH

Jul 85

U.S. Department of Commerce
National Technical Information Service
NTIS

PB85-245298

EPA/600/2-85/086
July 1985

INDUSTRIAL PROCESS PROFILES FOR ENVIRONMENTAL USE

Chapter 10a, The Plastics and Resins Processing Industry

by

Radian Corporation
McLean, Virginia 22102

EPA Contract No. 68-02-3994

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U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/2-85/086	2.	3. RECIPIENT'S ACCESSION NO. PB85 245298/AS
4. TITLE AND SUBTITLE Industrial Process Profiles for Environmental Use Chapter 10a: The Plastics and Resins Processing Industry		5. REPORT DATE July 1985
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Radian Corporation		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Radian Corporation 7655 Old Springhouse Rd. McLean, VA 22102		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO. 68-02-3994 68-02-3171
12. SPONSORING AGENCY NAME AND ADDRESS Water Engineering Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268		13. TYPE OF REPORT AND PERIOD COVERED Final Report (7/81 - 4/85)
		14. SPONSORING AGENCY CODE EPA/600/14

15. SUPPLEMENTARY NOTES

Contact Clyde R. Dempsey, (513)684-7502

16. ABSTRACT

This report contains a detailed analysis of the plastics and resins processing industry, which includes operations that convert polymers and resins into consumer products. Analytical elements include industry definition, raw materials, products, manufacturers, environmental impacts and occupational health impacts.

For the purpose of this analysis, the Plastics and Resins Processing Industry has been divided into eleven (11) segments, some of which are comprised of a number of different processes: calendering, casting, coating, compounding, extrusion, finishing, foam (expandable bead, extruded thermoplastic, multicomponent thermoset, and structural), laminating, molding (blow, compression, injection, reaction injection, rotational and transfer), reinforced plastics and thermoforming.

The IPPEU Chapter 10, 10a and 10b series is an update and expansion of material published in the 1977 report, IPPEU Chapter 10, the Plastics and Resins Industry, EPA-600/2-77-023j.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 431
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

DISCLAIMER

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Contract No. 68-02-3994 to Radian Corporation. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water systems. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. The Clean Water Act, the Safe Drinking Water Act, and the Toxic Substances Control Act are three of the major congressional laws that provide the framework for restoring and maintaining the integrity of our Nation's water, for preserving and enhancing the water we drink, and for protecting the environment from toxic substances. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Water Engineering Research Laboratory is that component of EPA's Research and Development program concerned with preventing, treating, and managing municipal and industrial wastewater discharges; establishing practices to control and remove contaminants from drinking water and to prevent its deterioration during storage and distribution; and assessing the nature and controllability of releases of toxic substances to the air, water, and land from manufacturing processes and subsequent product uses. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

This report covers the release of toxic materials to the environment and to the workplace during plastics processing. This report will be used in EPA's review of premanufacturing notices (PMN's).

Francis T. Mayo, Director
Water Engineering Research Laboratory

ABSTRACT

This document presents a detailed analysis of the plastics and resins processing industry, which includes operations that convert polymers and resins into consumer products. Analytical elements include industry definition, raw materials, products, manufacturers, environmental impacts, and occupational health impacts.

For the purpose of this analysis, the Plastics and Resins Processing Industry has been divided into 11 segments, some of which are made up of a number of different processes: calendering, casting, coating, compounding, extrusion, finishing, foam (expandable bead, extruded thermoplastic, multicomponent thermoset, and structural), laminating, molding (blow, compression, injection, reaction injection, rotational and transfer), reinforced plastics, and thermoforming.

The plastics and resins processing industry is made up of nearly 10,000 processors who produced an inventory of products valued at $37 billion in 1982. The industry is made up of many plants, most of which are small and located in or near urban centers. A compounded annual growth rate of 6 percent is projected through 1990.

Raw materials for the industry are the basic resins and additives described in IPPEU Chapter 10 (The Plastics and Resins Production Industry) and IPPEU Chapter 10b (Plastics Additives).

Products of plastics processing operations are used as substitutes for wood, metal, glass, leather, or natural fibers. Primary uses of plastics are packaging, construction, housewares, transportation, electric and electronic products, paints, furniture, appliances, and toys.

Plastics processing operations produce air emissions, wastewater, and solid waste resulting from both polymer and additive raw materials. Many processing operations do not produce all three waste streams. Particulate emissions made up of polymer and additive fines are possible during feeding, loading and blending of dry materials, part trimming, and grinding of thermoplastic scrap for recycle. Volatile emissions are possible from operations in which polymers and additives are heated.

Most process-related wastewater produced during polymer processing operations is generated from direct contact cooling of newly formed plastic products. Contamination of wastewater results from material washed or leached from the polymer.

Solid waste is produced by the collection of particulates from feeding, handling, and grinding operations and by trimming of parts. Thermoplastic scrap may be recycled, but thermoset scrap must be disposed of.

Worker exposure to harmful chemical substances and physical agents depends on the materials being handled, plant design, and effectiveness of engineering controls and personal protective equipment and clothing. These factors are essentially plant-specific and are highly variable throughout the industry.

This report was submitted in fulfillment of Contract No. 68-02-3994 by Radian Corporation under the sponsorship of the U.S. Environmental Protection Agency. This assignment covers the period October 1984 to April 1985.

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SECTION 1

INDUSTRY DESCRIPTION

INTRODUCTION

The Plastics and Resins Processing Industry is a large, diverse industry that uses polymers and resins produced by the plastics and resins production industry and produces a wide variety of plastic consumer products.

The polymer and resin raw materials* are supplied to the industry in the form of powders, pellets, and emulsions. The dividing line between polymer production and processing occurs during an operation termed compounding or formulation. Before being processed, all polymers and resins must be blended with the appropriate additives to make them well suited for their intended product use. Compounding operations can occur immediately following the polymer's production, just before or during the processing operation, or partially at both stages. Some large-volume producers of resins produce and process the polymer at the same facility. This is particularly true of fast, continuous process operations such as calendering and the casting of sheet materials. Typically, plastics are processed at locations other than those where the polymers and resins are produced. Plastics processors purchase resins that are best suited for their processing step from either the polymer producers or compounders.

Polymer processing operations appeared shortly after the discovery of the early plastics, since methods were needed to turn the plastics into usable items. The earliest processing operations were simple molding operations that were patterned after an early form of compression molding which was used to form billiard balls during the 1860's. In recent times, the discovery and development of polymers and processing operations have proceeded hand in hand. In some situations, copolymers and special formulations have been developed to make the plastic suitable for a desirable fabricating operation. Processing equipment is consistently being modified to accommodate various polymers and copolymers.

For the purpose of this analysis, the Plastics and Resins Processing Industry has been divided into 11 segments. Some of these segments are made up of a number of different processes. A delineation of the processing operations covered in this analysis is presented in Table 1. All of the

---

*The terms polymer and resin are frequently used interchangeably when describing the inputs of the plastic and resins processing industry. The term resin, which is more specific and is widely accepted, is used herein.

TABLE 1. POLYMER AND RESIN PROCESSING OPERATIONS

- Calendering
- Casting
- Coating
- Compounding (Formulation)
- Extrusion
- Finishing
- Foam
  - Expandable Bead Foams
  - Extruded Thermoplastic Foams
  - Multicomponent Thermoset Foams
  - Structural Foams
- Laminating
- Molding
  - Blow Molding
  - Compression Molding
  - Injection Molding
  - Reaction Injection Molding
  - Rotational Molding
  - Transfer Molding
- Reinforced Plastics
- Thermoforming

operations shown in Table 1 are concerned with the actual formation of the end product except for compounding and finishing. The compounding step, as indicated above, typically takes place immediately before the forming operations, whereas finishing involves further processing such as machining and decorating of the formed product.

More than 64 percent of the plastics products produced in the United States are processed by two major processing operations: Extrusion and Injection Molding. The following is a breakdown by percentage of the processing operations based on 1976 statistics:[72]

- Extrusion, 41 percent;
- Injection Molding, 23 percent;
- Blow Molding, 7 percent;
- Coating, 7 percent;
- Calendering, 3 percent;
- Foams, 2 percent; and
- All Others, 17 percent.

The listing for coatings includes those resins used for paints and primers.

Discussions of each of the polymer processing operations (in alphabetical order) follows in Sections 2 through 20. These include four forming operations (Sections 8 through 11), six molding operations (Sections 13 through 18), and nine other specific operations (Sections 2 through 7, 12, 19, and 20). The commentary on foaming and molding operations is preceded by introductory discussions.

In summary, the Plastics and Resins Processing Industry deals with those operations that convert polymers and resins supplied by the Plastics and Resins Production Industry into consumer products. The Plastics and Resins Production Industry is analyzed in Chapter 10 of the Industrial Process Profiles for Environmental Use (IPPEU). Other polymer products covered in the IPPEU series include Chapter 9 (The Synthetic Rubber Industry) and Chapter 11 (The Synthetic Fiber Industry).

INDUSTRY DEFINITION

The most recent data (June 1982) show that the plastics processing industry is made up of almost 9,400 processors with 10 or more employees. The 1977 Census of Manufacturers (the most recent survey presenting a complete set of industry statistics) showed that the industry employed 468,000 workers, an average of fewer than 50 employees per plant. The census data also indicate that more than 5,800 establishments in the industry had fewer than 20 employees. The four largest companies produced only 7 percent of the total industry shipments, which were valued at $37 billion. These plants produce a wide variety of products, and they range in size from small one-process and one-polymer operations to large, multifaceted facilities. Processing facilities tend to be located near the sales centers of the United States so that finished consumer products need not be transported over long distances. Therefore, a large percentage of the plastics processing facilities are located in Connecticut, Massachusetts, New York, New Jersey, Pennsylvania, Ohio, Michigan, Illinois, and California. Thus the industry is made up of many plants, most of which are small and located in or near urban centers.

The plastics processing industry has grown to its present size over the past 60 years. Much of this growth has taken place in the latter 10 to 20 years. In this period, the volume growth has been accompanied by a continuously expanding number of products requiring the use of new chemicals. As the plastics processing industry has grown, there has been an increasing interest on the part of Federal agencies that have regulatory responsibilities pertaining to this industry. Studies are continually being performed to determine the safety of certain plastic products (such as kitchenware) for food and drug packaging and consumer usage. The Environmental Protection Agency and the Occupational Safety and Health Administration have been concerned with a number of potential problems in the plastics processing industry and have investigated the potential effects of formaldehyde containing polymers and certain additives such as plasticizers and fillers.

Because of the inert nature of most plastics, the use and handling of the polymer itself and the related waste streams are generally not of primary concern (formaldehyde products being the exception). Most environmental and health effects problems that do arise during fabrication are due to the use of additives in the polymer formulations. Some of these additives are suspected carcinogens or are potentially hazardous if improperly handled.

All polymers that are produced must be processed in one way or another before they are useful as products. Thus it is reasonable to assume that the plastics processing industry in the United States will grow at a rate comparable to that of plastics production. At the present time, it is expected that the plastics industry will continue to grow at a compounded annual growth rate of 6 percent well into the late 1980's. Over the years, the actual rate will probably fluctuate up and down as a whole, depending on the overall state of the U.S. economy. An increased consumer demand for plastic products throughout the economy could lead to significant increases in processing. This is particularly applicable to the automotive and construction industries, where plastic goods are used extensively.

Furthermore, the plastics processing industry will most likely be unaffected by the influx of Middle Eastern polymers into the domestic plastics market. If the demand for plastics products exists, plastics processors will continue to operate, regardless of the origin of their polymer feed. The processing of polymers into final products will continue to be performed close to the consumer market centers because of the high cost of transporting finished products.

RAW MATERIALS

The raw materials for the Plastics Products Industry are the basic resins and additives. The resins comprise the highest volume input to an industry whereas additives are added in relatively small amounts but play an essential role in determination of the properties of the end products.

Resin Raw Materials

The resins that are primary inputs to the industry are shown in Table 2 along with the 1980 production volumes. The relationship between the various plastic processing operations and the resins commonly used in these operations are presented in matrix form in Table 3. The background on the manufacture of these materials is presented in IPPEU Chapter 10, Plastics and Resins Production Industry.

Major Plastic Additives

Most plastics forming operations incorporate additives to improve the processing and end use performance characteristics of polymers. The wide variety of chemicals used as plastics additives are classified by their function in the polymer; e.g., antioxidants, plasticizers, and UV absorbers. The following discussion gives an overview of 34 major plastics additives used in plastic processing operations. These major additives, listed in Table 4, were chosen for inclusion because they are:

- used in a wide variety of processing operations;
- used in high volume in plastics processing;
- representative of a large class of chemicals which perform a particular function; and/or
- known to pose a significant threat to the environment or workers involved in plastics processing.

The compounding section of this chapter details the methods used to incorporate additives into polymers and a summary of their functions. A comprehensive overview of polymeric additives and their functions is presented in Chapter 10b, IPPEU, Plastics Additives.

The additives discussed in this IPPEU chapter are used in a wide range of polymers and processes. Table 5 lists the 34 major additives used in particular polymer processing operations. Four factors influence the choice of additives for a particular polymer. These are:

- the intrinsic properties of the resin including its end use requirements;
- the compatibility of the resin and additives;
- the cost, mixing ease, and physical properties of the additive; and
- the additive's compatibility with the forming process.

It must be pointed out that these additives are not necessarily used for all polymers processed by a specific forming technique, nor are they utilized for all applications. For example, disposable garment bags produced from low density polyethylene by extrusion do not require an antioxidant, whereas

TABLE 2. PLASTICS AND RESINS PRODUCTION - 1980

Category	U.S. Production Thousand Metric Tons	Percent of Total
Acrylic Resins	247	1.5
Acrylonitrile-Butadiene-Styrene	416	2.6
Alkyd Resins	210	1.3
Amino Resins	589	3.7
Modified Polyphenylene Oxide and Polyphenylene Sulfide	56	0.4
Epoxy Resins	145	0.9
Fluoropolymers	6	<0.1
Phenolic Resins	686	4.3
Polyacetal	40	0.3
Polyamide Resins	158*	1.0
Polybutylene	7	<0.1
Polycarbonate	106	0.7
Polyester Resins (Saturated)	480	3.0
Polyester Resins (Unsaturated)	438	2.7
Polyethylene--High Density	1,997	12.5
Polyethylene--Linear Low Density	336	2.1
Polyethylene--Low Density	3,058	19.1
Polypropylene	1,689	10.6
Polystyrene (General Purpose and Impact)	1,599	10.0
Polyurethane Foam	762	4.8
Polyvinyl Acetate	304	1.9
Polyvinyl Alcohol	64	0.4
Polyvinyl Chloride	2,458	15.4
Polyvinylidene Chloride	78	0.5
Styrene-Acrylonitrile	47	0.3
Specialty Plastics	N/A	N/A
	15,976	100.0

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*The most recent polyamide production figures available are for 1979.

N/A - Not available.

TABLE 3. POLYMER AND PROCESS MATRIX[a]

Polymers Processing Operations	Acrylic Resins	Acrylonitrile-Butadiene-Styrene	Alkyd Resins	Amino Resins	Modified Polyphenylene Oxide and Polyphenylene Sulfide	Epoxy Resins	Fluoropolymers	Phenolic Resins	Polyacetal	Polyamide Resins	Polybutylene	Polycarbonate	High Density Polyethylene	Linear Low Density Polyethylene	Low Density Polyethylene (Includes EVA)	Polyethylene Terephthalate Polybutylene Terephthalate	Polypropylene	Polystyrene	Polyurethane	Polyvinyl Acetate	Polyvinyl Alcohol	Polyvinyl Chloride	Polyvinylidene Chloride	Styrene-Acrylonitrile	Unsaturated Polyester Resins
Injection Molding	●	●		●	●		●	●	●	●	●	●	●		●	●	●	●				●		●	●
Blow Molding	●	●							●			●	●	●	●	●	●	●				●			
Compression Molding			●	●		●	●	●														●			●
Transfer Molding			●	●		●		●																	●
Reaction Injection Molding																			●						
Rotational Molding									●	●		●	●		●							●			
Extrusion	●	●			●		●		●	●	●	●	●	●	●	●	●	●				●	●	●	
Calendering		●														●		●				●			
Casting	●					●		●		●					●		●		●			●			●
Thermoforming	●	●										●	●		●		●	●				●			
Expandable Bead Foams																		●				●			
Extruded Thermoplastic Foams		●											●				●	●				●			
Structural Foams		●			●							●	●				●	●							
Multicomponent Thermoset Foams				●				●											●						●
Reinforced Plastics	●	●	●	●	●	●	●	●	●	●		●	●	●		●	●	●	●					●	●
Coating	●			●		●		●		●					●	●	●		●	●	●	●	●		●
Laminating			●	●		●		●															●		

[a] This matrix presents those polymers which are most commonly used in each processing operation. Each process description presents a list of other less commonly used polymers.

TABLE 4. MAJOR PLASTICS ADDITIVES

Additive Class	Chemical
Antioxidants	2,6-Di-tert-butyl-4-methyl phenol (BHT) Trisnonylphenyl phosphite Dilauryl thiodipropionate
Blowing Agents	Azodicarbonamide Azobisisobutyronitrile Methylene chloride
Colorants	Carbon black Titanium dioxide Cadmium sulfoselenide Lead chromate Phthalocyanines Anthraquinone red Monoazo yellow
Flame Retardants	Antimony oxide Alumina trihydrate Trixylenyl phosphate Decabromodiphenyloxide Chlorinated paraffin wax
Heat Stabilizers	Tribasic lead sulfate Ba/Cd stearate Ca/Zn stearate
UV Stabilizers	2-Hydroxy-4-octoxy-benzophenone 2(2'-Hydroxy-5'-methylphenyl) benzotriazole Nickel dibutyldithio carbamate
Urethane Catalysts	Triethylene diamine Stannous octoate
Plasticizers	Dioctyl phthalate Diisooctyl phthalate Diisodecyl phthalate Tricresyl phosphate Di-(2-ethylhexyl)adipate
Reinforcing Agents	Glass fibers Asbestos Silica

TABLE 5. ADDITIVES USED IN PLASTICS PROCESSING[a]

Additive Class	Additive \ Process	Injection Molding	Blow Molding	Compression Molding	Transfer Molding	Reaction Injection Molding	Rotational Molding	Extrusion	Calendering	Casting	Thermoforming [b]	Expandable Bead Foams [c]	Extruded Thermoplastic Foams	Structural Foams	Multicomponent Thermoset Foams	Reinforced Plastics	Coating	Laminating
Antioxidants	2,6-Di-tert-butyl-4-methyl phenyl (BHT)	X	X				X	X							X		X	
	Trisnonylphenyl phosphite	X	X				X	X									X	
	Dilauryl thiodipropionate	X	X				X	X							X			
Blowing Agents	Azodicarbonamide												X	X				
	Azobisisobutronitrile												X					
	Methylene chloride												X	X	X			
Colorants	Carbon black	X				X	X	X	X						X		X	
	Titanium dioxide	X				X	X	X	X						X		X	X
	Cadmium sulfoselenide	X		X	X	X	X	X	X						X		X	
	Lead chromate	C				X		C										
	Phthalocyanines	X		X	X	X	X	X	X						X		X	
	Anthraquinone red	X						X										
	Monoazo yellow	X		X	X			X										
Flame Retardants	Antimony oxide	X	X	X	X		X	X	X						X	X	X	X
	Alumina trihydrate	X		X	X			X	X	X					X	X	X	X
	Trixylenyl phosphate	X						X	X									
	Decabromodiphenyl oxide	X	X				X	X										X
	Chlorinated paraffin wax	X	X				X	X	X	X							X	X
Heat Stabilizers	Tribasic lead sulfate	X						X	X								X	
	Ba/Cd Stearate	X					X	X	X	X							X	
	Ca/Zn Stearate	X	X					X	X	X							X	
UV Stabilizers	2-Hydroxy-4-octoxy-benzophenone	X						X	X						X		X	
	2(2'-Hydroxy-5'methylphenyl) benzotriazole	X						X										
	Nickel dibutyldithio carbamate	X						X										
Urethane Catalysts	Triethylene diamine					X									X			
	Stannous octoate														X			
Plasticizers	Dioctyl phthalate	X				X	X	X	X	X							X	
	Diisooctyl phthalate	X				X	X	X	X	X							X	
	Diisodecyl phthalate	X					X	X	X	X							X	
	Tricresyl phosphate	X					X	X	X								X	
	Di-(2-ethylhexyl)adipate	X				X	X	X	X								X	
Reinforcing Agents	Glass fibers	X		X	X	X		X		X					X	X		X
	Asbestos	X		X	X			X	X	X						X		
	Silica	X		X	X	X		X		X					X	X	X	

KEY: C = Coated lead chromate only.

[a] The additives listed here as being used in a particular processing step are documented in the literature sources sited for Table 5. Many other applications of these additives are possible.

[b] Formulating is performed in sheet production; therefore, thermoforming does not generally require additional additives.

[c] Expandable bead foams are generally formulated in polymerization.

other applications for this polymer and process typically incorporate a minimum of 0.01 percent antioxidant such as 2,6-di-tert-butyl-4-methylphenol (BHT).[131] Further it should be noted that polymer-additive formulations are generally considered proprietary information; therefore, it is possible that some additives used in processing are not detailed in the literature. This is particularly true for specialty applications of certain polymers and processes. A more detailed summary of the additive usage information is presented in Appendix A.

PRODUCTS

The products of plastics processing operations are the plastic goods and articles which are used in daily life. Plastics products have been designed as substitutes for wood, metal, leather, natural fibers, and glass in a wide variety of consumer and industrial applications. In many cases, these plastic products have actually replaced the original products since they can often be produced more economically and are often able to provide product qualities which cannot be acheived with other materials. Indeed, plastic products are now virtually indispensible in a wide variety of consumer and industrial markets including those shown below:

Quantity of Plastics for Major End Uses†

End Use	Millions of Pounds
Packaging	10,017
Construction	8,261
Housewares	2,474
Transportation	2,065
Electric and Electronic	1,852
Paints	1,512
Furniture	989
Appliances	964
Toys	627
Other Domestic Uses	12,875
Exports	4,475
Total	46,111

†Source: Kline's Guide to the Chemical Industry, 4th Edition

More specific information on the relationship between input resins and end products are shown on a series of Polymer-Process-Product diagrams included in Appendix B. The kind of information presented in these diagrams is shown in Figure 1 which shows the relationships between acrylonitrile-butadiene-styrene resins, manufacturing operations and products.

COMPANIES

The 1977 Census of Manufacturers shows that some 8,824 companies operate the 10,212 plants involved in the manufacture of plastic products from polymers and resins.

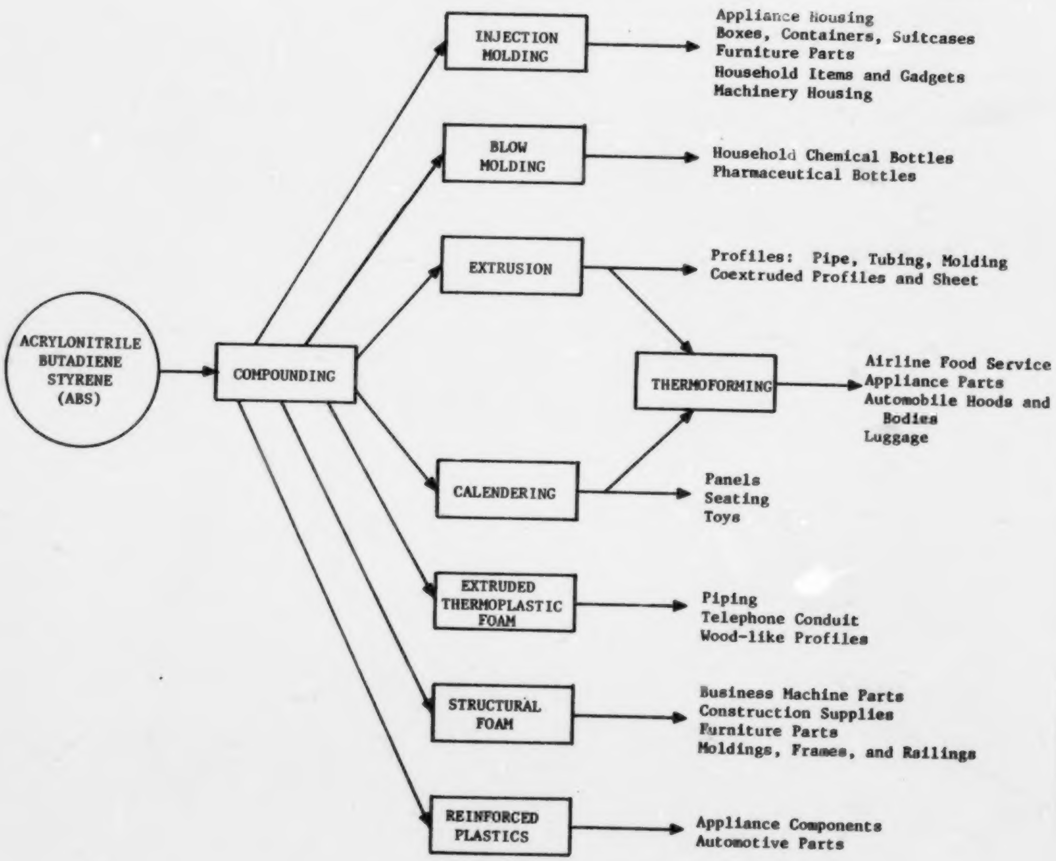

ACRYLONITRILE
BUTADIENE
STYRENE
(ABS)
COMPOUNDING
INJECTION MOLDING
BLOW MOLDING
EXTRUSION
THERMOFORMING
CALENDERING
EXTRUDED THERMOPLASTIC FOAM
STRUCTURAL FOAM
REINFORCED PLASTICS
Appliance Housing
Boxes, Containers, Suitcases
Furniture Parts
Household Items and Gadgets
Machinery Housing
Household Chemical Bottles
Pharmaceutical Bottles
Profiles: Pipe, Tubing, Molding
Coextruded Profiles and Sheet
Airline Food Service
Appliance Parts
Automobile Hoods and Bodies
Luggage
Panels
Seating
Toys
Piping
Telephone Conduit
Wood-like Profiles
Business Machine Parts
Construction Supplies
Furniture Parts
Moldings, Frames, and Railings
Appliance Components
Automotive Parts

Figure 1. Polymer-process-product (PPP) link.

The intermediate processing of resins after their manufacture may include processing by independent compounders and fabricators of semi-finished forms for further processing. The output from such intermediate processors plus unprocessed resins are raw materials for the producers of plastic end products. The end products manufacturers are of three types. About 20 percent of the plastic products are produced by the companies that manufacture the resins. The balance is produced by 5,600 independent processors of custom or proprietary products and captive producers operating 9,100 captive plants controlled by the manufacture of automobiles, appliances, furniture, etc.

The net effect of this mode of operation is that resins and associated chemicals are handled in plants with wide variety in type of management, level of supervision, and the adequacy of occupational health and safety practices.

ENVIRONMENTAL IMPACT

Plastics processing operations as a whole produce air emissions, wastewater, and solid waste resulting from both the polymers and additives. Many processing operations do not produce all three waste streams. Table 6 presents a summary of the emissions and waste streams produced by all of the plastics processing operations. A detailed description of the emissions from each operation can be found in the specific process descriptions contained in Sections 2 through 20.

Air Emissions

The air emissions from plastics processing operations consist of both particulate and volatile emissions. All of the processing operations have the potential to produce particulate emissions during the feeding, loading and blending of dry polymers and additives, the trimming of parts, and/or the grinding of thermoplastic scrap for recycle. Additional particulates are produced during pelletizing operations. Pelletizing and finishing operations generally produce polymer particulates which contain the compounded additives. In most cases, the additives are encapsulated in an inert plastic and do not present the same hazard that they would if alone. Loading, blending, and processing operations may produce individual polymer and additive particulates or additives bound in a polymer matrix. The additive alone is generally of greatest concern. Properly designed and operated mixing and grinding equipment should keep particulates to a minimum. Additional particulates are controlled by various standard particulate control techniques such as fabric filters and wet scrubbers.

All processing operations have the potential to release volatile emissions. Volatile emissions are generated during the heating of the polymer in molds, chambers, and injection or extrusion cylinders. This includes preheating and curing operations. Emissions are also released when large polymer surface areas are exposed as is the case in extrusion, calendering, and coating operations.

TABLE 6. PLASTICS PROCESSING EMISSIONS SUMMARY

	Air Emissions		Waste-water	Solid Waste
	Volatiles	Particulates		
Injection Molding	X	X	a	X
Blow Molding	X	X	a	X
Compression Molding	X	X	a	X
Transfer Molding	X	X		X
Reaction Injection Molding	X	X		X
Rotational Molding	X	X	a	X
Extrusion	X	X	X	X
Calendering	X	X	a	X
Casting	X	X	X	X
Thermoforming	X	X	a	X
Expandable Bead Foam	X	X	X	X
Thermoplastic Foam Extrusion	X	X	X	X
Structural Foam	X	X	a	X
Multicomponent Thermoset Foam	X	X		X
Reinforced Plastics	X	X		X
Coating	X	X	X	X
Laminating	X	X		X
Finishing	X	X	X	X
Compounding	X	X	X	X

---

[a] These operations most often use indirect cooling water; however, some applications may use direct contact cooling water.

The composition of the volatile emissions from these operations depends upon the processing technique which is used. Most emissions will contain volatilized monomer, plasticizer, other additives, and decomposition products. Decomposition products occur when the processing temperature reaches that temperature at which the polymer begins to decompose. Fluoroplastics, polyesters, polyethylenes, and polyvinyl chloride are the polymers which are most susceptible to decomposition at typical processing temperatures. Special formulations of these polymers which include heat stabilizer additives are used to limit decomposition. Each process description in this document details the potential decomposition products for the specific polymers used in the process.

The major environmental concern with plastics additives is in the area of air emissions. Most additives used are solids or liquids capable of particulate and aerosol formation. Others are liquids which may form volatile emissions during processing. Casting and other thermoset processing operations such as transfer molding, compression molding, and laminating have the potential to release volatilized catalysts, solvents, and cure reaction by-products. Foaming operations release excess expansion and foaming agents usually nitrogen, CO_2, or halocarbons. Table 7 presents the potential particulate and volatile emissions for the major plastics additives.

Various additive modifications such as concentrates, liquids, pellets, and pastes are utilized to reduce air emissions. Colorants are the heaviest users of these modifications, but similar modifications are used with other additives. In addition to reducing particulate emissions, these modified additives reduce mixing requirements, inventories, and downtime for polymer or additive changes.

Wastewater

Most process related wastewater produced during polymer processing operations is generated from the direct contact cooling of newly formed plastic products. Wastewater of this nature is routinely produced during pelletizing (compounding and extrusion); profile, pipe, and tube cooling (extrusion); wire and cable coating (extrusion); casting; expandable bead and extruded thermoplastic foams; coating; and cooling during machining operations (finishing). A number of the other processes utilize indirect cooling water to cool the newly formed plastics. Occasionally, due to the requirements of a specific product, direct contact cooling is used during injection molding, blow molding, compression molding, rotational molding, calendering, thermoforming, and structural foam production. In most plastics processing operations, the direct contact cooling water is recycled, thus reducing the actual amount of wastewater produced.

Wastewater produced during direct contact cooling will contain suspended polymer, additives, filler particulates, and soluble constituents, and in some casting and fiber spinning applications, solvent. Contamination of wastewater results from material washed or leached from the polymer. Additives may contribute to wastewater by both these mechanisms; however, the leaching process is a major concern in many forming operations. Since leaching of additives is of concern in both wastewater and solid waste

TABLE 7. AIR EMISSIONS FOR ADDITIVES

Additive Class	Chemical	Particulates	Volatiles	Comments
Antioxidants	2,6-Di-tert-butyl-4-methyl Phenol (BHT)	X	X	Some BHT may be vented when processing temperatures exceed 265°C.
	Trisnonylphenyl phosphite	L	X	Readily volatilizes at processing temperatures for film and fibers.
	Dilauryl thiodipropionate	X		
Blowing Agents	Azodicarbonamide	X	X	Gas composition is 65% N_2, 32% CO, and 3% CO_2. NH_3 may be present.
	Azobisisobutyronitrile	X	X	Gas composition is mainly N_2. Toxic residue-i.e., tetramethylsuccinonitrile may volatilize.
	Methylene Chloride	X	X	Boiling point = 40.1°C.
Colorants				Masterbatches, pellets, low dusting formulations and color concentrates are commonly used to reduce particulate emissions.
	Carbon Black	X		
	Titanium Dioxide	X		

(continued)

TABLE 7 (continued)

Additive Class	Chemical	Particulates	Volatiles	Comments
Colorants (Cont.)	Cadmium Sulfoselenide	X		
	Phthalocyanines	X		
	Lead Chromate	X		
	Anthroquinone Red	L		
	Monoazo Yellow	L		
Flame Retardants	Antimony Oxide	X		Not effective without complete dispersion. High density of this compound reduces dusting. Reduced dusting grades available.
	Alumina Trihydrate	X		Good dispersion essential. Reduced dusting forms available.
	Trixylenyl Phosphate	L		
	Decabromodiphenyl Oxide	X		Decomposes at 423°C.
	Chlorinated Paraffin Wax	X		Specially formulated solids have low heat stability. Solids have decomposition temperatures at 250-300°C. (Boiling point varies dependent upon molecular weight of the wax.)

(continued)

TABLE 7 (continued)

Additive Class	Chemical	Particulates	Volatiles	Comments
Heat Stabilizers	Tribasic Lead Sulfate	X		
	Ba/Cd Stearate	X		
	Ca/Zn Stearate	X		
UV Stabilizers	2-Hydroxy-4-octoxy-benzophenone	X	X	Tends to volatilize at high processing temperatures.
	2(2'-Hydroxy-5'-methylphenyl)benzotriazole	X	X	
	Nickel dibutyldithio carbamate	X	X	
Plasticizers	Dioctyl Phthalate	L	X	4.5% volatilizes at 87°C in 24 hours.
	Diisooctyl Phthalate	L	X	4.3% volatilizes at 87°C in 24 hours.
	Diisodecyl Phthalate	L	X	1.3% volatilizes at 87°C in 24 hours.
	Tricresyl Phosphate	L	X	1.0% volatilizes at 87°C in 24 hours.
	Di-(2-ethylhexyl)adipate	L	X	13.9% volatilizes at 87°C in 24 hours.

(continued)

TABLE 7 (continued)

Additive Class	Chemical	Particulates	Volatiles	Comments
Reinforcing Agents	Glass Fibers	X		The extent of particulate emissions is largely dependent on the form and forming method (e.g., roving, fabric, cord or loose fibers, laminating, spray-up, hand lay up, etc.).
	Asbestos	X		Vacuum vents are used to compact polymer - asbestos melt in extrusion.
	Silica	X		

L = Liquid aerosols may form.

Sources: Allbee, Nancy, "Update: Flame Retardants Part 1: Inorganic Additives," Plastics Compounding, July/August 1981, p. 89.

Allbee, Nancy, "Update: Flame Retardants Part 2: Organic Additives," Plastics Compounding, September/October 1981, p. 95.

Katz, Harry S. and John V. Milewski, Handbook of Fillers and Reinforcements for Plastics, 1978, p. 425.

Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 18, p. 140.

Encyclopedia of Polymer Science and Technology, Vol. 14, p. 125-145.

Nass, Leonard I., Encyclopedia of PVC, 1977, p. 813.

disposal, this topic will be discussed separately following the overview of solid wastes produced in processing.

Solid Waste

Solid waste is produced during plastics processing operations primarily by the collection of particulates from feeding, handling, and grinding operations, and by the trimming of parts. Calendering and coating operations produce plastic scrap in the form of uncontrolled drippings from the calender or coating knife. During casting and coating operations which use plastisols, contaminated plastisol will comprise another waste stream. In a number of the thermoplastic processing operations, the amount of plastic scrap which must be disposed of is greatly reduced by the recycling of ground scrap to the polymer feed.

Most of the solid waste produced by plastics processing operations contains primarily polymers and small quantities of plasticizers, fillers, and other additives. Plastics processed without additives are essentially inert materials which pose little or no solid waste disposal problems; however, when additives are incorporated into the plastic, leaching of the additives during landfill operations must be considered. The following section presents the leaching concerns for disposal of additive plastics.

Leaching of Additives

Leaching may occur through water contact with the polymer or through interactions with other wastes. Many additives which cannot be extracted with water, are readily extracted by other solvents. These may be present in landfills, and thus increase the leaching rate. Most additives are chosen for their compatibility with the polymer, and migration of the additives to the surface of the polymer is minimized. Thus, in a carefully compounded and processed plastic, leaching should be limited to the polymer surfaces. The extent of leaching will be dependent upon the concentration of the incorporated additive, the polymer with which it is blended, and the contact time. Leaching of plasticizers and colorants has received most extensive study. Plasticizers may present significant leaching problems because high concentrations are present in the resin and compatibility may be low with some plasticizers. Colorants, particularly those containing heavy metals, have been studied due to concerns over the adverse health effects presented by heavy metals.[186, 220]

WORKER EXPOSURE AND EXPOSURE CONTROLS

Employees in plastic and resin compounding and fabricating operations may be exposed to a variety of hazardous chemical substances and physical agents, including:

- Residual monomer or comonomers,
- Metallic pigments,
- Silaceous additives or asbestos,
- Volatile decomposition products,
- Volatile additives,

- Nuisance dust from polymer grinding, and
- Noise.

Contaminants of concern generated in each compounding and fabrication operation included in this document are discussed in individual sections. A general discussion of exposure and exposure controls is given below.

Employee Exposure

Employees involved in raw materials handling, materials transfer and mixing and blending operations are most likely to encounter elevated workplace levels of residual monomer, comonomer and additives. Workers in downstream operations may contact volatile additives and decomposition products; pelletizing, grinding, machining, and bagging operations may generate large quantities of polymer fines which constitute (at the least) a nuisance dust hazard. Individual additives such as asbestos may represent a more serious hazard. Operations throughout a fabrication plant may be noisy: mixers, blenders, conveyors, rollers, pelletizers, and grinders may generate high noise levels.

A NIOSH study indicates that, with a few exceptions, exposures in plastics compounding and fabrication operations remain uncontrolled.[205] The NIOSH study, although based on a limited number of compounding and fabricating plants, was the only source of data found in readily-available literature. Some of the more common reported problems leading to overexposure are discussed in the following paragraphs.[205]

Inadequate general ventilation - many of the toxic materials used are in the form of very fine powders, with particle sizes below 5 microns mean aerodynamic diameter. When these particles become airborne, they will remain suspended for extremely long times unless removed by an adequate general ventilation system.

Poor housekeeping - in most cases, there is no scheduled cleanup in areas where toxic materials are used. In essentially all cases, when cleanup is undertaken, dry methods such as sweeping are used. Further, employees frequently use compressed air to rid their work areas and their clothing of settled dust. Both of these cleaning methods are inappropriate in terms of dust control; it is probable that no cleanup is preferred to these methods.

Improper storage and handling of toxic additives - few compounding facilities had segregated and/or limited access storage areas for toxic additives. Frequently, pallet loads of additive bags and containers were positioned in large, open storage areas where they may be torn or ripped by forklifts. Further, spills of dry material will readily become airborne due to frequent equipment or personnel movement. A common practice of handling empty additive bags is to compact them by hand in a non-exhausted area, dump them in open trash barrels, and/or leave them on the floor until picked up and disposed of as other trash. Any of these practices are large sources of potential exposure.

Poor work practices - when using toxic, dry materials, proper work practices are critical to successful dust control. Examples of poor practices include opening additive containers outside of the hoods provided for dust containment, sloppy handling of additive powders, poor opening procedures for bags, and general improper use of local exhaust systems. Most times, additives are received in 50 pound to 100 pound bags although batch recipes normally require much smaller quantities. This requires an expanded amount of short-weight additive preparation.

Nonexistent or poorly designed local ventilation systems - most plants have either table top or walk-in hoods where additives can be weighed in accordance with batch recipe requirements. Many are of poor design, including: 1) inadequate design airflows; 2) ineffective placement and sizing of exhaust slots; 3) low duct tranpsort velocities which lead to plugging; and, 4) too shallow hood depths. Further, many hoods are swept with excessive cross drafts, either from pedestal fans or open windows. The hoods designed to exhaust the additive dumper operation into the mixers and/or blenders are similarly poorly designed.

Most mixers, blenders, hoppers, feed chutes, and conveyor belts are not provided with any local ventilation. A substantial amount of dust is generated when seals wear out and fittings are inadequate.

Poor ventilation system maintenance - with dusts, particularly where the exhaust loading is heavy, maintenance of the local ventilation system is essential. If duct transfer velocities are not maintained at 17.8 to 20.3 m/s (3500 to 4000 fpm), dust particles will not remain entrained in the air flow. Most of the time, this occurs at branch elbows, and the duct gradually becomes obstructed and air flows are choked or at least diminished relative to design values.

Most local ventilation systems designed to remove dust have particulate filters in line to allow exhausting of relatively clean air to the atmosphere. With heavy dust loading, the filters will rapidly become plugged, due to the increased system static pressure (resistance). The actual air flow will decrease to values well below the value specified on design. It was a frequent observation that the filters are not monitored to determine when maintenance is required.

Noise exposure - in general, excessive noise exposure is common around mixers, blenders, pelletizers and dicers, where noise levels may range from 100 to 115 dBA. Many times, these noise sources are difficult to control via isolation or enclosure.

Employee Monitoring

Actual contaminant levels in individual plants can be determined only through implementation of a comprehensive employee monitoring program. To obtain monitoring data, employees typically wear personal sampling pumps or monitoring badges throughout an average work shift.

Personal sampling pumps can be used to collect samples for many different airborne contaminants. The sampling pump is worn by the employee and is connected to an appropriate sample collection medium which is positioned in the employee's breathing zone. NIOSH has developed sampling techniques with recommendations for collection medium, pump flow rate, and sample volume. Additional sampling techniques can be found in the Hygienic Guide Series for individual substances, published by the American Industrial Hygiene Association, and in NIOSH criteria documents for individual substances.

Monitoring badges (passive dosimeters) are available for measuring employee exposure to organic vapors and some inorganic gases. These badges are easy to use and allow samples to be collected by non-technical personnel. Subsequent analysis is done by gas chromatography (organic vapors) or colorimetric methods (inorganic gases).

Battery-operated personal dosimeters are available for monitoring employee exposure to noise. The monitoring unit is worn by the employee during the work-day. The device reads out in percent of allowable exposure. Some monitors are available which allow charting of noise-exposure levels encountered during the day.

If it is not possible for the employee to wear the monitoring equipment, personal exposure measurements can be taken in the employee's immediate environment. These measurements are then used to calculate a daily average or an exposure peak. Monitoring equipment suitable for this type of investigation includes a wide range of direct-reading instruments as well as sample collection devices. For example, a sound level meter can be used to measure noise levels at several representative work locations for an individual. These measurements, along with an estimate of time spent in each location, can be used to calculate the employees daily exposure. Similarly, contaminant concentration levels can be measured using colorimetric indicator tubes. Daily exposure can be calculated on the basis of time spent at each typical concentration level.

Employee Exposure Controls

In a 1978 report, NIOSH concluded that effective examples of engineering controls were not widespread in the plastics forming industry.[205] Numerous recommended controls exist in the literature, but most have not been demonstrated in the industry.

Engineering Controls--

The American Conference of Governmental Industrial Hygienists (ACGIH) has recommended local exhaust ventilation for dusts generated during mixing, grinding and bagging operations.[205] Specific controls include:

- Ventilated charge booths for mixers,
- Discharge hoods for resin charging and product packaging,
- Canopy hoods for calender rolls,
- Enclosed pneumatic conveyors for resin particle transfer, and

- Flexible, moveable metal hose systems for non-permanent bagging or loading operations.

Despite some effort at noise abatement, NIOSH reports that overexposure to noise is a significant problem in plastics compounding and fabrication operations.[205] Pelletizers and dicers are the primary noise sources. Reportedly, some compounding plants have enclosed noisy equipment in concrete block rooms.[205] Although these structures theoretically provide adequate attenuation through transmission loss, their actual effectiveness is often decreased by improper use (i.e. openings too large; doors left open). Noise abatement measures applied directly to equipment are generally ineffective because noise sources are numerous and complex, and the controls interfere with frequent maintenance operations.[205]

Acoustically-treated baffles may have potential in attenuating equipment noise levels. NIOSH reports that enclosure of a dicer with acoustically-treated ceiling, walls, doors and windows provided an attenuation of about 22 dB.[205]

Personal Protective Equipment--

Where engineering controls are insufficient, personal protective equipment or clothing is necessary to reduce exposure levels to reported safe levels. The degree of protection necessary depends on the types of hazardous materials in the workplace and the conditions under which an employee may be exposed.

Dermal protection minimizes or prevents contact of the skin with potentially hazardous materials which may be absorbed into the body, cause contact burns (chemical or physical), skin lesions, or carcinomas. Use of a removable protective layer also provides a means for removing contaminants from employees before they leave work, thus minimizing exposure to persons outside the plant. Coveralls, gloves, aprons and other dermal protection devices must be constructed of materials which will not allow hazardous material penetration. Eye protection is necessary for employees involved in operations such as handling input chemicals, taking process samples, performing maintenance and machining or grinding. ANSI Z87.1 gives specifications for protective eyewear used in a variety of situations.

On many fabrication operations, it is not feasible to reduce noise levels emitted from an operation to levels below that allowed for an eight hour exposure. However, employees can be protected through limiting the duration of their exposure in the area and through the use of hearing protection devices.

Personal protective devices for hearing protection are either insert-type or muff-type. Ear protection devices may be used either independently in normal high noise areas or in combination for maximum protection in extreme noise areas.

Respiratory protection may be necessary to reduce employee exposure both to nuisance dust, hazardous additive materials such as asbestos or silica, and volatile monomer or decomposition products. Selection of the proper type of respiratory protection may be a complex task. This is due to multiple potential hazards encountered in particular activities, as well as the large number and variety of respiratory protective devices available.

Respirators are of either the air-purifying type or atmospheric supplying type. Air-purifying respirators are limited in that they can only be used in atmospheres with sufficient oxygen. Additionally, they are specific for particular substances or classes of substances. In contrast, atmosphere supplying respirators provide the breathing atmosphere and are not dependent on either of the two above factors. However, atmosphere supplying respirators are sometimes cumbersome because they must have an air supply attached.

Common air-purifying respirators draw air through cannisters or cartridges to clean the contaminant from the air before it is taken into the facepiece for breathing. Typical cartridges or cannisters are specific for organic vapors, acid gases, or dusts, mists, and fumes. Air purifying respirators with various facepiece styles (full facepiece, half facepiece) have upper limits of contaminant concentrations, established by NIOSH and used in areas or operations where the exposure level is known to be below the ceiling allowed for the respirator, and where no chance exists of encountering an oxygen deficient atmosphere. Additionally, this type of respirator should be used only in areas where no significant concentrations of toxic gases are present for which the respirator may be ineffective.

In oxygen-deficient atmospheres, employees should wear atmosphere supplying respirators with full facepieces. Either a supplied air respirator or self contained breathing apparatus (SCBA) is an appropriate choice. Supplied air (air line) respirators may be preferable for this type of work if an air supply connection is available and if the work is limited to a single area without need for movement over great distances. A standard supplied air respirator (preferably positive pressure or pressure demand), certified by NIOSH or MSHA for work in this type of atmosphere is recommended for use in areas where exposure levels remain below those "immediately dangerous to life or health".

A typical SCBA unit is bulky, heavy, and usually can supply air for a maximum of 30-60 minutes. This type of respirator should be used for emergency responses to unknwon conditions, or entry and work where movement over large areas is required.

Administrative Controls--

Employee training is very important. Workers should be knowledgeable about the nature of the safety and health hazards in the plant and the provisions that are available to them for protection against the hazards. They must be educated in the proper use and reason for each protective device or procedure required.

Another important administrative control is the development of standard operating procedures and safe work practices. Employees should be provided with written instructions for job performance and personal protective equipment use. Demonstrations of competency should be required periodically.

SECTION 2

CALENDERING

FUNCTION

The calender was developed nearly 100 years ago for applications in the processing of natural rubber. It is now widely used in the plastics processing industry to produce uniform quality film and sheet at high production rates. Calendering operations squeeze pliable thermoplastic between a series of rotating rolls to produce polymer film and sheet. Calendered film and sheet is generally produced in widths of up to about 2 m (80 in) and in the range of 0.005 to 0.13 cm (0.002 to 0.05 in) thickness.[133] Commercial calender rolls can be very large, up to 0.9 m (3 ft) in diameter by 2.4 m (8 ft) long, and are capable of tremendous production rates (up to 91 m/min.).[177]

In terms of capital investment for machinery and equipment, calendering is one of the most expensive processing operations.[61] The large calendering rolls must be precision ground to assure quality product. Calendering operations must be carefully controlled in order to keep performance within close tolerances and to prevent excessive scrap formation. Large calendering rolls have the tendency to bend from the tremendous forces associated with calendering. This is usually overcome by roll crossing, crowning, and bending in order to produce a film or sheet of uniform thickness. Beta-ray gauges are frequently employed to assure uniform thickness by controlling calender functions.[177]

Due to its capability to produce uniform quality product at high production rates, calendering is economically favorable to film and sheet extrusion for a number of applications. This is particularly true for applications which use polyvinyl chloride (PVC) such as flooring, paneling, and pool and pond liners. Flexible and rigid PVC, totaling 283,000 metric tons in 1980, comprises the largest amount of input polymer to calendering operations.[133]

INPUT MATERIALS AND PRODUCTS

Input materials to calendering operations include thermoplastic resins and formulation additives such as lubricants, stabilizers, plasticizers, and colorants. Flexible and rigid polyvinyl chloride compounds are the most commonly used materials for the manufacture of calendered products. Processors also use acrylonitrile-butadiene-styrene (ABS), polyethylene, and polystyrene for various film applications.[10]

Most often, resin formulations are blended just prior to calendering. Lubricants and plasticizers are particularly important in calendering formulations in order to allow the film to flow over the calender rolls and to prevent cracking as the film solidifies. Additive formulations are uniquely determined in order to provide the properties dictated by the product use. Table 8 displays the relationship between polymer type, formulation, and products of calendering operations. More information on major plastics additives used in calendering is presented in the Industry Description section of this document.

Typical formulations for calendering PVC resins are shown below:[158]

Material	Parts by Weight
PVC Resin (Scon S.5410)	100
Dioctyl Phthalate (plasticizer)	40
Barium/Cadmium/Zinc Complex (stabilizer)	2
Epoxidized Soya Bean Oil	5-8
Lubricant	0-1

Material	Parts by Weight
PVC/PVDC Copolymer (CS 100/30)	100
Dioctyl Phthalate (plasticizer)	50
Cadmium Stearate	2
Lubricant	0-0.5
Phenyl Salicylate (Salol)	1

The first formulation shown is used to produce clear sheet or film. The second formulation is useful for producing transparent, unsupported film, with good processing properties and light resistance.

PROCESS DESCRIPTION

Calendering operations generally consist of five operation units: mixing, calendering, take-off, cooling, and trimming. Each of these units will be discussed separately in this process description and are illustrated in the block diagram in Figure 2.

The thermoplastic resin is transferred from storage facilities through a sieve to a high shear mixer or mill. Ribbon blenders and/or Banbury mixers are often used for this operation along with intensive mixers such as Henschel or Littleford.[61] The plasticizers and other additives are charged in appropriate ratios to the mixer. Heat is supplied to soften the polymer mix and to promote uniform blending. Mixing is usually performed around 80°C (176°F).[19] The polymer, now having the consistency of soft clay, is fed through a metal detector to identify any metal which could damage the expensive calender rolls.[134] Extruders frequently are used to perform the mixing operations, thereby replacing the blenders and/or mixers.[134] Particulate emissions are generated during the transfer, weighing, and initial mixing of the dry ingredients. Scrap polymer drippings may result from mixing operations as well as volatile plasticizer emissions.

TABLE 8. INPUT MATERIALS AND PRODUCTS OF CALENDERING OPERATIONS

Polymer	Formulation	Products
Acrylonitrile-Butadiene-Styrene (ABS)	Dry resin 2-4 hours at 82-93°C (180-200°F) in dehumidifying air hopper before processing	Panels Seats Toys
Polyethylene		
LDPE	Antioxidants Antiblocking Agents	Film Diced Sheet
HDPE	Resin	Film for packaging applications
Polypropylene		
Polystyrene	Resin	Film for packaging applications
Polyvinyl Chloride/Polyvinyl Acetate Copolymer (PVC/PVAc)	Copolymer with: Colorants Fillers Plasticizers Stabilizers	Flooring sheet and tiles
Polyvinyl Chloride (PVC)	Resin with: Antioxidants Antistatics Colorants Fillers Flame Retardants Fungicides Heat Stabilizers Impact Modifiers Lubricants Plasticizers Reinforcers UV Stabilizers	Building and construction applications including flooring, paneling, pool, pond, and roof liners Transportation applications including auto upholstery and trim, and tops (thermoformed) Packaging (large applications) utilizing sheet and film Electrical Tapes Furniture and Furnishing including shower curtains, upholstery and trim, wall coverings, waterbed sheet, window shades, blinds, and awnings

(continued)

TABLE 8 (continued)

Polymer	Formulation	Products
PVC (Continued)		Consumer and institutional goods including baby pants, book bindings, coffin liners, credit cards, decorative films, tapes, and labels, footwear, handbags, cases, and luggage, inflatables, sporting and recreation goods, tablecloths, placemats, hospital sheets, printer's blankets, raincoats, draperies, and countertops
Polyvinylidene Chloride	Colorants Plasticizers	Food packaging wrap

Sources: Agranoff, Joan (ed). Modern Plastics Encyclopedia 1981-1982, pp. 4, 58, 90, and 100.

Dubois, J. Harry and Frederick W. John, Plastics, 1981, p. 238.

Eldin, R. A., and A. D. Swan, Calendering of Plastics, 1971, pp. 17, 98.

Grayson, Martin (ed). Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Edition, Vol. 16, p. 415.

Meienberg, J. T., "Calendering," Modern Plastics Encyclopedia 1981-1982, p. 243.

Nass, L. I. Encyclopedia of PVC, 1977, p. 126.

"Plastics 82," Modern Plastics, January 1982, p. 55.

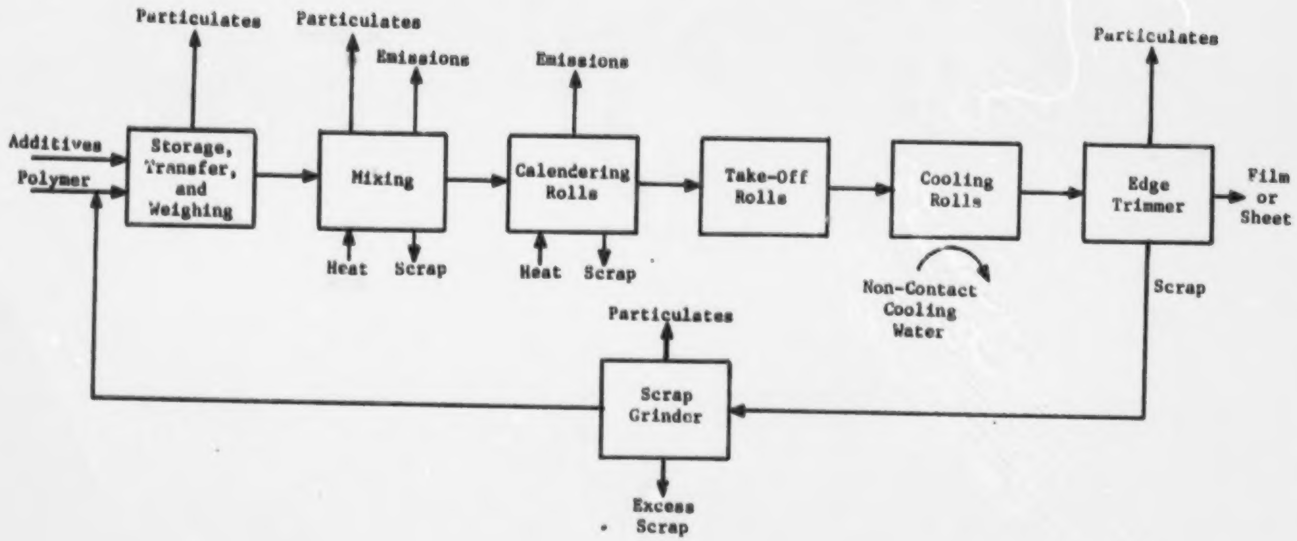

Particulates
Particulates
Emissions
Emissions
Particulates
Additives
Polymer
Storage, Transfer, and Weighing
Mixing
Calendering Rolls
Take-Off Rolls
Cooling Rolls
Edge Trimmer
Film or Sheet
Heat
Scrap
Heat
Scrap
Non-Contact Cooling Water
Scrap
Particulates
Scrap Grinder
Excess Scrap

Figure 2. Calendering.

The soft polymer leaves the mixing operation and is fed either manually or automatically to the main unit of the calendering process - the calender. The calender is usually comprised of three to five cast iron rolls, which squeeze the softened polymer into a sheet or film of desired width and thickness. The arrangement of the calender rolls is determined by the product requirements as are the number of rolls and the roll spacings. The clearance between rolls is progressively decreased in order to slowly reduce the thickness and increase the width of the sheet or film. Most roll arrangements are adjustable to allow versatility in production methods. Figure 3 presents diagrams and characteristics of the four basic calender roll arrangements.[61]

The calender rolls are heated in order to maintain the pliability of the forming sheet. The most commonly used heating medium is high pressure hot water at approximately 1.7 x 10^6 Pa (250 psi) and 100 to 200°C.[61] Some applications do utilize high pressure steam at 6.9 to 13.8 x 10^5 Pa (100 to 200 psi) and 120 to 185°C.[61] When very high roll temperatures are required, electrically heated oil is used as the heat source.[61] The temperatures of the rolls are usually maintained such that a 5 to 10°C gradient exists between each roll.[61] Since formulations usually adhere to the hotter roll, an increasing temperature gradient aids in the processing of the film. Figure 4 illustrates a typical roll temperature gradient for processing PVC.

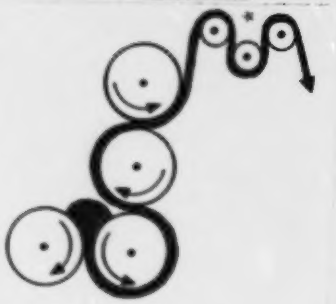
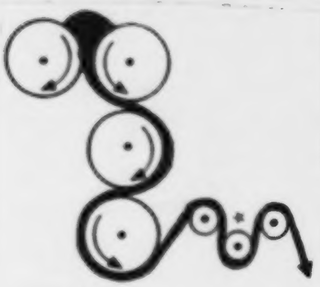
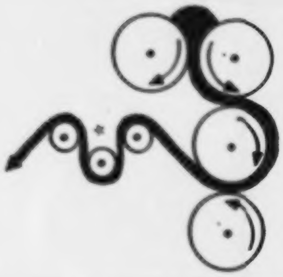
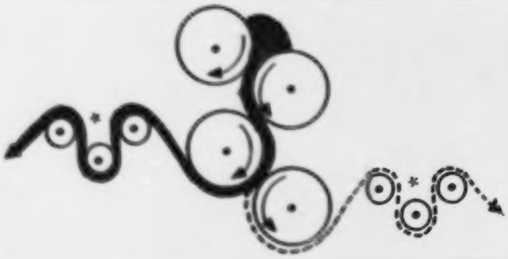
The calender rolls are usually powered by individual d.c. motors and gear trains so that each roll can be adjusted to suit the sequence necessary to produce film of the required thickness. Typical roll speeds range from 15 to 46 m/min (50 to 150 ft/min) and can go as high as 91 m/min (300 ft/min) for very thin film applications.[61] Depending on the surface of the final calendering rolls, the film or sheet can be smooth, matted, or embossed.

Plastic scrap is produced by drippings from the calender rolls. Due to the large film surface area exposed during the calendering sequence, volatile emissions can be released from the hot plastic.

Film and sheet is removed from the calendering rolls by a group of take-off or "stripper" rolls. These rolls, usually three in number, are typically 20.3 cm (8 in.) in diameter and are arranged so that the sheet or film follows an S shape configuration as seen in Figure 3. The take-off rolls run faster than the calender rolls to impart orientation or stretch to the sheet or film.[72]

The take-off rolls feed the sheet or film to a series of indirectly water cooled cooling rolls. The sheet or film is gradually cooled by a series of 2 to 10 such rolls.[61] The cooled product is then fed to the edge-trimmer where it is trimmed to product specifications. Scrap from the edge-trimmer is usually ground and recycled to the polymer feed. Particulates are produced by the trimming and grinding operations.

Calendering is also used to polymer coat materials such as paper and fabric. The process is similar to that described above except that fabric or paper is fed into the calendering rolls as the plastic film is formed. The plastic and fabric are tightly bonded together by the heat and force of the rolls and emerge from the cooling rolls as a single composite sheet. A simplified diagram of calender coating is shown in Figure 5.

TYPE	CONFIGURATION	CHARACTERISTICS
L-Calender		• Offset roll on the bottom • Take-off rolls on the top
Inverted L-Calender		• Offset roll on the top • Take-off rolls on the bottom
F-Calender		• Offset roll on the top • Take-off rolls are in the middle on the offset side
Z-Calender		• Two rolls are offset • Take-off on bottom of either side

*Take-off rolls

Figure 3. Basic calendering configurations.

Sources: Frados, Joel, Plastics Engineering Handbook, 1976, p. 357.

Meienberg, J. T., "Calendering," Modern Plastics Encyclopedia, 1981-82, p. 243.

Roll	Temperature
1	150°C
2	155°C
3	160°C
4	165°C

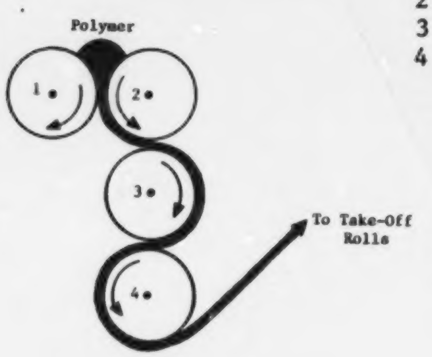

Polymer
1
2
3
4
To Take-Off Rolls

Figure 4. Typical calendering roll temperature gradient for PVC.

Sources: Baird, R. J., Industrial Practices, 1971, p. 139.

Elden, R. A. and A. D. Swan, Calendering of Plastics, 1976, p. 17.

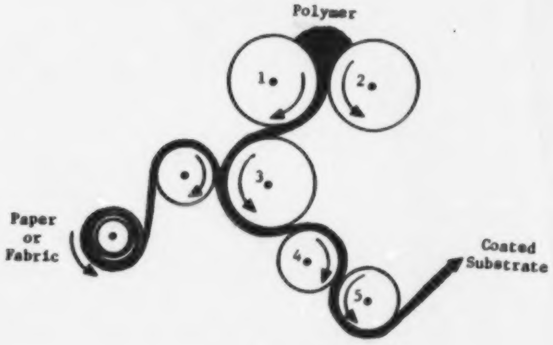

Polymer
1
2
3
4
5
Paper or Fabric
Coated Substrate

Figure 5. Calender coating roll formation.

Source: Elden, R. A. and A. D. Swan, Calendering of Plastics, 1976, p. 17.

OPERATING PARAMETERS AND UTILITY REQUIREMENTS

The temperature of the mixing unit, calendering rolls, and cooling rolls must be carefully maintained to assure production of quality product. The mixing unit and calender roll temperature are maintained by auxiliary heating units which circulate steam, hot water, or hot oil. The hot fluid is usually circulated through drilled passages in a triple pass pattern in order to control for optimum processing temperature. Mixing is usually performed around 80°C (176°F). Calender roll temperatures must be constant and uniform over the width of each roll. Automatic temperature controls and thermocouples are routinely used to assure proper temperature distribution.[134] Roll temperatures range from 150 to 250°C (302 to 482°F).[133] The cooling rolls are served by a chilled-water system or a plant cooling tower.[133]

Each calender roll has its own electronically controlled drive to assure uniform speed at the high production rates and thin films produced today.[134] The drive horsepower required in calendering operations depends on the number of rolls, roll diameter, face width, surface speed, and polymer formulation. Calenders for rigid PVC require higher horsepower for a given roll speed than those processing flexible PVC, since rigid formulations contain less plasticizers and are, therefore, less pliable than flexible PVC.[177] Typical drive horsepower requirements for a four roll flexible PVC calender range from 410 to 560 KW (550 to 750 hp.).[133]

WASTE STREAMS AND EMISSIONS

Calendering operations produce air emissions and solid waste. No wastewater is directly generated by the calendering operation, however, wastewater may be produced when wet scrubbers are used to control particulate emissions. Table 9 presents a summary of the point source emissions from calendering operations. Emissions and wastes are discussed in more detail in the text below. The waste streams and emissions from major plastics additives used in calendering operations are detailed in the Industry Description section of this document.

Air Emissions - All calendering operations have the potential to produce particulates and volatile emissions. Particulates are produced during the storage, transfer, weighing, and mixing of the resin and additives. Trimming and scrap grinding operations also produce particulates. These particulates consist of polymer, plasticizer, colorant, and other additive particles. Particulates can be controlled by various standard control devices such as fabric filters and wet scrubbers.

Volatile emissions may be liberated from polymer mixing and from the large sheet surface exposed during calendering operations. Such emissions would be comprised of volatilized plasticizers and other additives, residual monomer, and decomposition products. Decomposition products occur when excess heat causes the polymer to decompose. Table 10 presents a table of decomposition products which can occur when the various calendering input polymers are exposed to high temperatures. The temperatures above which decomposition products are likely to be formed are also listed. Calendering formulations usually include stabilizers to inhibit decomposition product formation and plasticizers which do not volatilize easily at the process temperature.

TABLE 9. CALENDERING POINT SOURCE EMISSIONS

	Air Emissions						Solid Waste		
	Particulates			Volatiles					
	Polymer	Plasticizer	Additives	Monomer	Plasticizer	Decomposition Products	Polymer	Plasticizer	Additives
Storage, Transfer, Weighing	X	X	X						
Mixing	X	X	X	X	X				
Calendering Rolls				X	X	X	X	X	X
Edge Trimmer	X						X	X	X
Scrap Grinder	X						X		

TABLE 10. DECOMPOSITION PRODUCTS

Polymer	Highest Processing Temperature (°C)†	Decomposition Temperature (°C)§	Decomposition Products
ABS	250	300	*
Polyethylenes	250	100	Ketone carbonyl groups form due to oxidation
Polypropylene	250	300	*
Polystyrene	250	300	*
PVC	250	100	HCl
Polyvinylidene Chloride	250	300	*

---

*Decomposition products are not formed at or near calendering processing temperatures.

†This is the highest possible temperature reached by the normal calendering of all formulations of the polymer listed.

§This is the lowest temperature at which decomposition products begin to form.

Wastewater - Calendering operations only utilize water in the indirect cooling of the cooling rolls. Therefore, no wastewater streams are expected to be produced by the calendering process. Wastewater may be produced if particulate emissions are controlled by wet scrubbing. Such a waste stream would contain suspended solids such as polymer and colorants, and may include soluble constituents such as plasticizers.

Solid Waste - The calendering process generates plastic drippings from the mixer and the calender, and scrap from trimming operations. Drippings and contaminated scrap cannot be reused and must be disposed of as solid waste. Trimmed scrap from coating operations can rarely be reused since it is a composite. Occasionally composite scrap can be ground and used to produce heavy sheet products with rough surfaces.[191] Thermoplastic trim can usually be ground and recycled to the polymer feed.

The disposal of most plastic scrap from calendering operations should present no problems since plastic scrap is characteristically inert. Problems may be presented by the disposal of scrap from formulations for flexible PVC containing large quantities of the plasticizer dioctyl phthalate (DOP). DOP is currently suspect as a carcinogen as a result of test data which indicates that it may cause cancer in rats.[160]

WORKER DISTRIBUTION AND EXPOSURE

The number of workers employed in a plastics calendering operation depends on the operation's capacity and complexity. Worker distribution has been estimated by correlating major equipment manhour requirements with the process flow diagram shown in Figure 2:

Unit	Workers/Unit/8-Hour Shift
Calendering	0.5
Trimming	0.25

Fugitive emissons from calendering operations may result in employee overexposure to a variety of chemical substances and physical agents. Factors affecting employee exposure include:

- Type of resin formed,
- Type of additives incorporated into resin,
- Type of equipment used,
- Condition of equipment (i.e. extent to which regularly-scheduled maintenance is performed), and
- Plant configuration (i.e. manual or automated operations).

Thermoplastic resins typically formed by calendering include ABS, polyethylene terephthalate, polybutylene terephthalate, polystyrene and polyvinyl chloride.[10] Potential for employee exposure exists in five operation units: mixing, calendering, take-off, edge-trimming, and scrap grinding. Major chemical substances and physical agents estimated to be associated with each of these operation units are shown in Table 11. Toxicity information and Occupational Safety and Health Administration (OSHA) regulatory status for the

TABLE 11. CALENDERING EMISSIONS AND RELEASE POINT ESTIMATION

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Mixing	Fugitives	Polymer particulates - nuisance dust
		[1]Colorants - carbon black
		- titanium dioxide
		- Cd sulfoselenide
		- phthalocyanines
		[1]Flame Retardants - antimony oxide
		- alumina trihydrate
		- trixylenyl phosphate
		- chlorinated paraffin wax
		[1]Heat Stabilizers - tribasic lead sulfate
		- Ba/Cd stearate
		- Ca/Zn stearate
		[1]Plasticizers - dioctyl phthalate
		- diisooctyl phthalate
		- diisodecyl phthalate
		[1]Reinforcers - asbestos
	Mixing machines materials handling	Noise
	β-ray gauge	Ionizing radiation
Calendering	Fugitives	[2]Residual monomer - acrylonitrile
		- butadiene
		- sytrene
		- ethylene glycol
		- 1,4 butanediol
		- dimethyl terephthalate
		- terephthalic acid
		- vinyl chloride

(continued)

TABLE 11 (continued)

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Calendering (Cont.)	Fugitives (Cont.)	[1]Volatile plasticizers - dioctyl phthalate - diisodecyl phthalate Decomposition products - ketone carbonyls (from polyethylene) - HCl (from PVC)
	Calendering rolls	Noise Heat stress
Take-off	Take-off rolls	Noise
Edge-trimming	Fugitives	Polymer particulates
Scrap Grinding	Fugitives	Polymer particulates

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[1] Specific additives listed are those documented in the literature. Many other additives may be used, depending on product formulation specifications.

[2] Primary monomers used to produce the thermosets typically calendered. Other monomers or comonomers may also be present.

substances and agents in Table 11 are summarized in Appendix C of this document and discussed in detail in Chapter 10, IPPEU, Plastics and Resins Production Industry, and Chapter 10b, IPPEU, Plastics Additives.

SECTION 3

CASTING

FUNCTION

Thermoplastics and thermosets are used in casting operations to produce a wide variety of products ranging in weight from a few grams to several tons. The plastic may be a molten polymer or a partially polymerized monomer solution with the cure being effected by the use of catalyst, heat, or a combination of the two depending upon the polymer type and formulation. The long cure times and large amount of manual labor required in casting processes usually make casting too expensive for large volume production runs. Casting is, therefore, preferred over continuous molding processes for small volume runs of specialty or prototype parts.

In the plastics processing industry, the term casting is used rather loosely to describe a wide variety of processes including fluidized bed coating, dip coating, rotational molding, hand lay-up, embedment casting, and film casting. For the purposes of this document, casting processes involve liquid plastics which are allowed to cure at atmospheric pressure in a mold or on a mold surface. Therefore, some of the aforementioned processes are more appropriately described under the molding (rotational molding), coating (fluidized bed and dip coating), and reinforced plastics (hand lay-up) sections of this report. Sometimes preforming processes are termed casting operations. Since such processes employ fiber reinforcements, they will be discussed in Section 19, Reinforced Plastics. The following casting operations will be presented in this section:

- Pot Casting
- Slush and Dip Casting
- Chilled Film Casting
- Solvent Casting
- Cell Casting
- Continuous Casting

INPUT MATERIALS AND PRODUCTS

Input materials to casting operations include resins, formulation additives, fillers, and release agents. Both thermoplastic and thermoset resins can be utilized in casting operations. Commonly cast thermoplastics include acrylics, nylons, and polyvinyl chlorides. Thermosets which are commonly cast include epoxy resins, polyesters, phenolics, and polyurethanes. Historically, the majority of cast resins have been thermosets; however, recent developments in thermoplastic formulations have greatly expanded the uses of thermoplastics in casting operations.[23] These developments have included the formulation of catalysts which allow the thermoplastics to be cast in place without the use of high pressure and temperature.

The properties of the input resins can be modified and enhanced by the use of appropriate additives such as plasticizers, colorants, and UV absorbers. Some resins require the addition of catalysts to effect the proper cure. Additive formulations are uniquely determined in order to provide the properties dictated by the product use. Table 12 displays the relationship between polymer type, casting process, formulation, and products for each polymer commonly utilized in casting operations. Polyacetal and polycarbonate are occasionally used in casting operations.

Fillers are often used in casting formulations to enhance the usefulness of the cast plastic part. Fillers can be used to reduce the total weight of the product, improve heat conduction, act as reinforcement, and/or reduce the total cost of the product by reducing the amount of polymer used per item. The type and amount of filler used is determined by the product specifications. Table 13 presents a list of fillers commonly used in commercial casting operations.

Casting molds are often treated with release agents before they are allowed to come in contact with the resin. This facilitates the removal of the part from the mold after curing. Release agents are particularly important when dealing with resins such as nylon which do not exhibit as large a cure shrinkage as many other resins. A list of release agents commonly used in casting operations is shown below:

CASTING MOLD RELEASE AGENTS

Cellophane
Fluorocarbon Spray
Lecithin
Mineral Oil
Paste Wax
Polyvinyl Alcohol
Silicone
Stearic Acid

Sources: Milby, R. V., Plastics Technology, 1973, p. 432.
Wallis, B. L., "Casting," Encyclopedia of Polymer Science and Technology, Vol. 3, p. 7.

More detailed information on major plastics additives used in casting is presented in the Industry Description section of this document.

TABLE 12. INPUT MATERIALS AND PRODUCTS OF CASTING OPERATIONS

Polymer	Casting Operation	Formulation	Products
Acrylics	Pot Casting	Monomer-polymer syrup - premixed methylmethacrylate monomer containing: Catalysts Chain Transfer Agents Colorants Flame Retardants Modifiers Plasticizers Release Agents UV Stabilizers	Novelties Plaques Knobs Embedments Dentures Instrument panel
	Cell Casting		Sheet such as Lucite®, Plexiglas®, and Acrylite® Tubing and rods Radar plot boards Landing light covers Aviation windows
	Continuous Casting		Sheet for production at signs and displays Furniture Canopies Skylights Sanitary ware Outdoor table tops Solar glazing panels
Epoxy	Pot Casting	Epoxy Resins Catalysts Diluents Fillers Flame Retardants Hardners Lubricants Plasticizers Reinforcers	Automotive molds Aircraft molds Delicate electric component encapsulation Costume jewelry Patterns Parts requiring little cure shrinkage
Nylon 6	Pot Casting	Predrying of monomer and additives required Nylon monomer (epsilon caprolactam) containing: Activator Catalyst Colorants Fillers Reinforcers	Bearings Gears Heavy duty parts Parts to be machined Rollers Bushings

(continued)

TABLE 12 (continued)

Polymer	Casting Operation	Formulation	Products
Phenolic	Pot Casting	Phenolic resins containing: Catalysts Colorants Fillers Lubricants Plasticizers Reinforcers	Transparent models of mechanical parts for stress evaluation Billiard balls Jewelry Imitation marble Sheet, rod, tube Profile shapes Tooling patterns Umbrella handles Cigarette holders Beads and buttons
Polyamide	Pot Casting	Fatty polyamide and low molecular weight epoxy resin with: Catalysts Colorants Fillers Flow Control Agents	Electrical embedments Plastics tooling
Unsaturated Polyesters (Allyl Resins)	Pot Casting	Allyl diglycol carbonate resin containing: Peroxide Catalysts Flame Retardants Reinforcers	Optical products
		Diallyl phthalate containing: Peroxide Catalysts Flame Retardants	Electrical encapsulation
Polyester	Pot Casting	Liquid polyester resin containing: Catalysts Colorants Fillers Fungicides Inhibitors Promotors Reinforcers Reodorants Thixotropes UV Absorbers Viscosity Depressants Wax or Flexibilizer	Novelties and art forms Table and sink tops Window sills Cultured marble Displays Furniture and cabinet parts Embedding scientific specimens Sheet Jewelry

(continued)

TABLE 12 (continued)

Polymer	Casting Operation	Formulation	Products
Polyethylene	Chilled Film Casting	Low density polyethylene containing: Antiblocking Agents Antioxidants	High clarity films
Polypropylene	Chilled Film Casting	Molten polypropylene homopolymer or ethylene-propylene copolymer containing: Antioxidants Antiblocking Agent	High clarity films
Polyurethane	Pot Casting	Prepolymer containing: Catalysts Colorants Curing Agents Plasticizers Promoters	Seals and gaskets Decor and trim Furniture parts Housewares Prototype tools Shoe soles Skate wheels
	Solvent Casting	Solvent	
Polyvinyl Chloride	Slush and Dip Casting	Plastisol dispersion formed from: Polyvinyl chloride powder (.02 - 2 microns) Antioxidants Antistatic Agents Colorants Fillers Flame Retardants Fungicides Heat Stabilizers Impact Modifiers Lubricants Plasticizers Reinforcing Agents UV Stabilizers Viscosity Depressants	Novelties Flexible molds Fish lures Toys Seals and gaskets Housewares Doll heads Boots and gloves Coin purses and eye glass cases Gloves Small bottle crown caps Complex electronic circuit harnesses Clay pipe seals Gaskets
	Solvent Casting	Organosol dispersion formed by adding solvents to plastisol dispersion formulas	Sheet and film

(continued)

TABLE 12 (continued)

Sources: Bikales, Norbert M. (ed). Encyclopedia of Polymer Science and Technology, Vol. 10, p. 609.

Frados, Joel, ed., Plastics Engineering Handbook, 1976, pp. 447-449.

Gage, P. E., "Casting of Nylon," Modern Plastics Encyclopedia, 1981-1982, p. 248.

Grayson, Martin (ed). Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Edition, Vol. 15, p. 386.

Harper, C. A., Handbook of Plastics and Elastomers, 1975, pp. 8-56.

Levy, S. and J. H. DuBois, Plastics Product Design Engineering Handbook, 1977, p. 181.

Luskin, L. S., "Casting of Acrylic," Modern Plastics Encylopedia, 1981-1982, p. 246.

May, C. A. and Y. Tanaka, Epoxy Resins, 1973, p. 533.

Milby, R. V., Plastics Technology, 1973, pp. 430, 436.

Nass, Leonard I., Encylopedia of PVC, 1977, p. 437.

Penn, W. S., PVC Technology, 1971, p. 419.

Schwartz, Seymour S. and Sidney H. Goodman, Plastics Materials and Processes, 1982, p. 230.

Wallis, B. L., "Casting," Encyclopedia of Polymer Science and Technology, Vol. 3, p. 7.

TABLE 13. FILLERS UTILIZED IN CASTING OPERATIONS

Aluminum Powder
Asbestos
Calcium Carbonate
Clay (Kaolin)
Diatomaceous Earth
Expanded Volcanic Rock
Fumed Silica (Cab-O-Sil®)
Glass: Flake, Ground,
    Microspheres, and
    Milled Fibers

Iron Filings
Marble Dust
Phenolic Microspheres
Plaster
Slate Dust
Steel Wool
Talc
Thermoplastic Pellets
Vermiculite
Walnut Shell Dust
Wood Flour or Sawdust

Sources: Gage, P. E., "Casting of Nylon," *Modern Plastics Encyclopedia, 1981-1982*, p. 248.

Milby, R. V., *Plastics Technology*, 1973, p. 433.

Examples of typical casting formulations are given below:[129, 183]

Material	Parts by Weight
Methyl Methacrylate Polymer	23
Methyl Methacrylate Monomer	77
Sunoco 4412 Wax (lubricant)	0.2
Glycol Bis(mercaptoacetate) (chain transfer agent)	0.25
t-Butyl Monopermaleate	0.5
Water	2.0
Calcium Carbonate (filler)	150

Material	Parts by Weight
Epoxy Resin (Shell Chem. Co.)	100
Silica, 1,000 mesh (filler)	150
2,4,6-Tris(dimethylaminomethyl) phenol (Rohm and Haas) (catalyst)	2
Nadic Methyl Anhydride (Allied Chem. Corp.) (cure agent)	83

PROCESS DESCRIPTION

The six types of casting processes which will be discussed in this section are pot casting, slush and dip casting, chilled film casting, solvent (solution) casting, cell casting, and continuous casting. For each process, waste streams shown in the process diagrams are discussed in this section.

Pot Casting is the simplest form of casting and it is used to produce a wide variety of products. Common pot cast polymers include acrylic, alkyl resins, diallyl phthalate, epoxy, nylon, phenolic, polyester, and polyurethane.

During pot casting a liquid polymer or a monomer solution is poured into an open mold where it is allowed to cure. The pot cast part is cured by the addition of heat in an oven, exothermically by means of a catalyst, or by a combination of both methods. Emissions may be liberated during the curing of catalyzed systems. Cast products may cool by either air or contact cooling water. Parts which are allowed to open air cool [29, 136] do not produce contact cooling water waste streams. Products are removed from the mold either by hand, air blasts, or ejector pins. Some cast products require trimming and are often buffed, machined, or tumbled to impart the proper product appearance. Solid thermoplastic scrap can be recycled in pot casting operations; however, thermoset scrap must be disposed of as a solid waste. A block diagram of a pot casting process is shown in Figure 6.

Molds used for pot casting can be very inexpensive and are often made from plaster, glass, wood, metal, and other plastics. Silicone elastomer is commonly used as a mold material since its pliability allows for easy part release and exact detail duplication. Fillers and reinforcements, as presented in Table 13, are often utilized in pot casting. Typical cure shrinkages of 7 to 12 percent volumetrically [177] facilitate removal of the products from the molds.

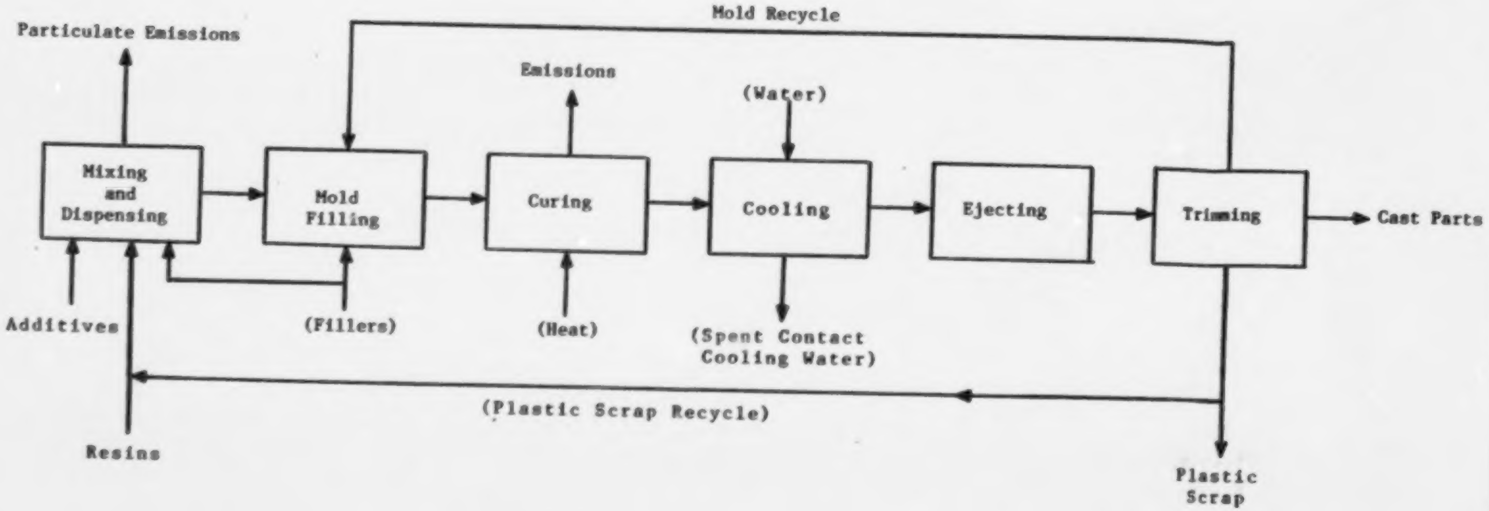

Particulate Emissions
Mold Recycle
Emissions
(Water)
Mixing and Dispensing
Mold Filling
Curing
Cooling
Ejecting
Trimming
Cast Parts
Additives
(Fillers)
(Heat)
(Spent Contact Cooling Water)
(Plastic Scrap Recycle)
Resins
Plastic Scrap

Figure 6. Pot casting.

Parenthesis indicate that the stream is not present in all post casting operations.

Typical pot cast products include novelties, plaques, knobs, embedments, electrical encapsulations, optical products, bearings, gears, jewelry, billiard balls, seals and gaskets, housewares, and furniture parts.

Slush and Dip Casting involves the use of liquid plastisol (fine particle polyvinyl chloride (PVC) dispersed in plasticizers such as dioctyl phthalate). These plastisols are viscous at room temperature and can be made in a wide range of colors. In slush casting, a roughly measured amount of plastisol is poured into a hollow mold which has been preheated to approximately 177°C (350°F).[10] The mold is rotated quickly so as to cover all inside surfaces and after a specific period of time, usually three to five minutes, [10] excess plastisol is poured out into a storage vat for future reuse. Mold temperature is carefully controlled to avoid degradation of the plastisol. The thickness of the hollow part is determined by the amount of time the plastisol remains in the mold. The mold is then placed in an oven and is maintained at 177 to 232°C (350 to 450°F) for several minutes to complete fusion.[10] After heating, the molds are usually water cooled, either by immersion or with a spray mist, after which they are opened and the part is ejected. A waste cooling water stream is thus produced in a typical slush casting process. Slush molding can easily be operated as a fully automated assembly line process. Typical slush cast products include housewares, novelties, doll heads, fish lures, and toys.

In dip casting, a mold is preheated to approximately 177°C (350°F) and dipped into the liquid plastisol for three to five minutes.[10] A polymer coating fuses around the mold during immersion. The coated mold is then placed in an oven at approximately 177°C (350°F) for 5 to 15 minutes [10] to complete fusion. The part is often cooled with water sprays, thereby producing a cooling water waste stream. The part is then stripped from the mold usually by an air blast. Typical dip cast products include novelties, flexible molds, boots, gloves, coin purses, and eye glass cases.

Molds used for slush and dip casting are usually made of aluminum, the surface of which is often treated with a mold release agent. A variation of dip casting exists when the mold becomes part of the product (i.e., tools with coated handles). However, this process is considered a coating process and is discussed in the coating section of this document.

Scrap plastisol is rarely produced during slush and dip casting since, during slush casting, excess plastisol is poured back into the storage vat for reuse and, in dip casting, the plastisol remains in the blending/coating vat with the mold being dipped into it. In this sense, plastisol liquid is continually reused. Care must be taken during these operations to avoid contamination due to dirty molds. Block diagrams of slush and dip casting are shown in Figure 7. Fluidized-Bed Coating is a process very similar to dip casting except that finely powdered polymer is used instead of plastisol. This process is discussed in the coating section of this document.

Chilled Film Casting is a casting method for the production of non-oriented, thin, polymer films. Polypropylene homopolymer, propylene-ethylene copolymer, and low density polyethylene are commercially utilized in this process to produce film. The most common form of chilled film casting is

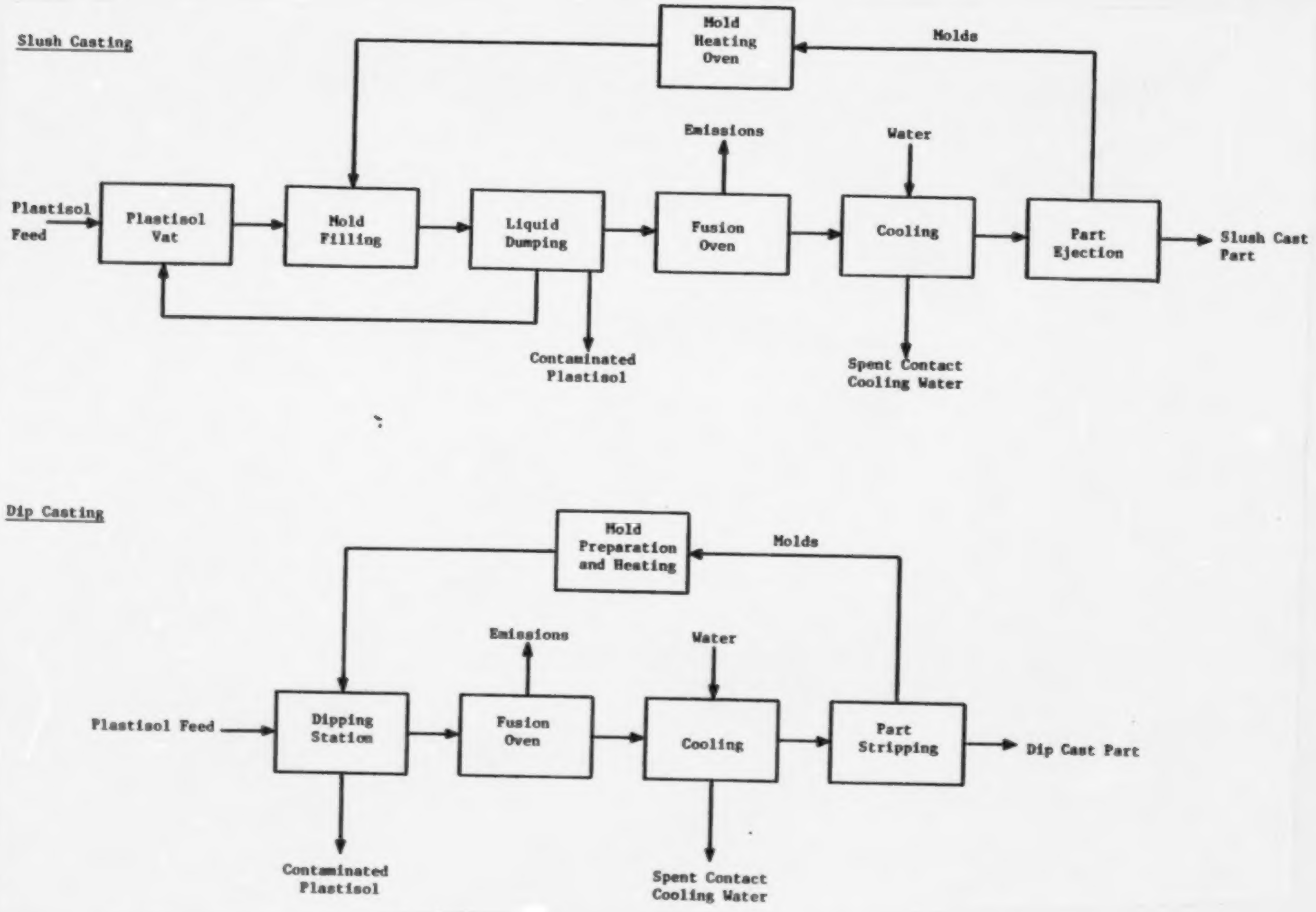

Slush Casting
Mold Heating Oven
Molds
Emissions
Water
Plastisol Feed
Plastisol Vat
Mold Filling
Liquid Dumping
Fusion Oven
Cooling
Part Ejection
Slush Cast Part
Contaminated Plastisol
Spent Contact Cooling Water
Dip Casting
Mold Preparation and Heating
Molds
Emissions
Water
Plastisol Feed
Dipping Station
Fusion Oven
Cooling
Part Stripping
Dip Cast Part
Contaminated Plastisol
Spent Contact Cooling Water

Figure 7. Slush and dip casting.

termed chill roll casting (CRC).[2] In chill roll casting, the formulated polymer is extruded (see Section 6 - Extrusion) through a slot die onto a rotating, chilled, polished roll. The movement of the roll draws the molten resin away from the die without significantly stretching or orienting the film. The extrudate solidifies into a film as it passes over the chilled roll surface. The film is trimmed as necessary and wound onto rolls.

A less commonly used chilled film casting method is termed tubular water bath casting (TWB). A rotating circular die is used to extrude downward a vertical tube of formulated polymer over a water cooled mandrel. A water bath quenches the cast film, thereby producing a cooling water waste stream. The film is then slit, trimmed, and wound onto rolls.

Chill casting operations produce high clarity film products. Since this process normally uses thermoplastics, trimmings from chill cast films can generally be reground and recycled to the extruder feed. A block diagram of a chill casting process is shown in Figure 8.

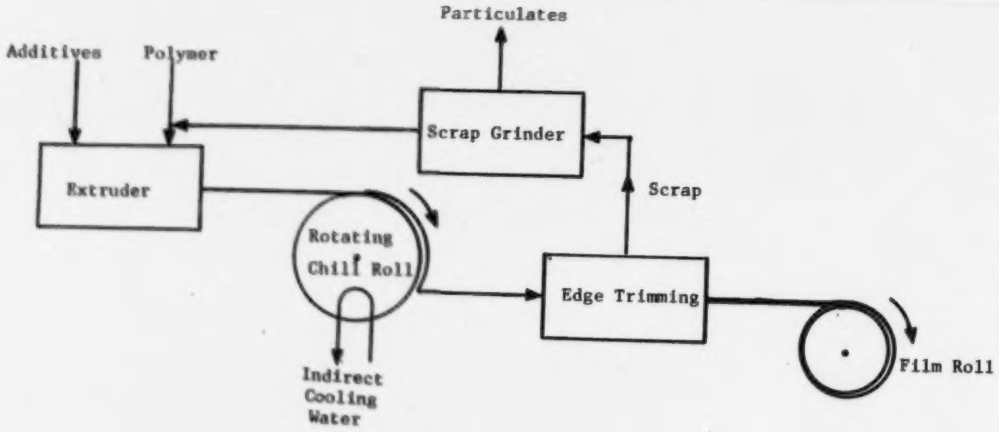
Solvent Casting, often referred to as solution casting, is used for the production of film and sheet. Polyvinyl chloride (PVC) organosols are the most commonly utilized polymers for this process. Organosols are formed by dispersing finely powdered PVC in plasticizer and organic solvents. Organosols are often prepared by modifying plastisols with organic solvents such as naptha diluents, diisobutyl ketone, or isophorone.[130]

The solution is poured onto a rotating drum or an endless belt which passes through an oven. The surface of the drum or belt is usually highly polished or patterned to effect the proper film surface. The solvent is evaporated in the oven in carefully programmed heat zones which are designed to prevent blister formation. A relatively solvent-free polymer film leaves the oven. After air cooling, the film is trimmed as necessary and is wound onto rolls or cut to product specifications. Although the evaporated solvent is recovered and recycled, the solvent casting process is still complex and costly. The solvent evaporation also presents an explosion hazard.[209] It is not anticipated that this process will see growing applications in the future due to the use of volatile solvents. A diagram of solvent casting is shown in Figure 9.

A process similar to solvent casting is used to coat cloth and paper substrates with plastisols. This process, called plastisol coating, will be discussed in the coating section of this report.

Cell Casting is utilized to produce sheet, tubes, and rods. Acrylic sheet is cast in the thickness range of 0.8 to 10.8 cm (.03 to 4.25 in.).[122] A premeasured amount of liquid acrylic, consisting of a small amount of polymer in a monomer and additive solution, [177] is poured between two sheets of polished or tempered plate glass that are slightly larger than the desired acrylic sheet product. The glass cell is held together by tubing and spring clips which can respond to shrinkage during the cure. The glass cells are then placed horizontally [209] in an oven for curing. Ovens generally operate on a programmed heating cycle which starts at 45°C (113°F) and is raised to 90°C (194°F).[122] The oven cycle on the average continues for 12 to 16 hours

Chill Roll Casting


Particulates
Additives
Polymer
Scrap Grinder
Extruder
Scrap
Rotating Chill Roll
Edge Trimming
Film Roll
Indirect Cooling Water

Tubular Water Bath Casting

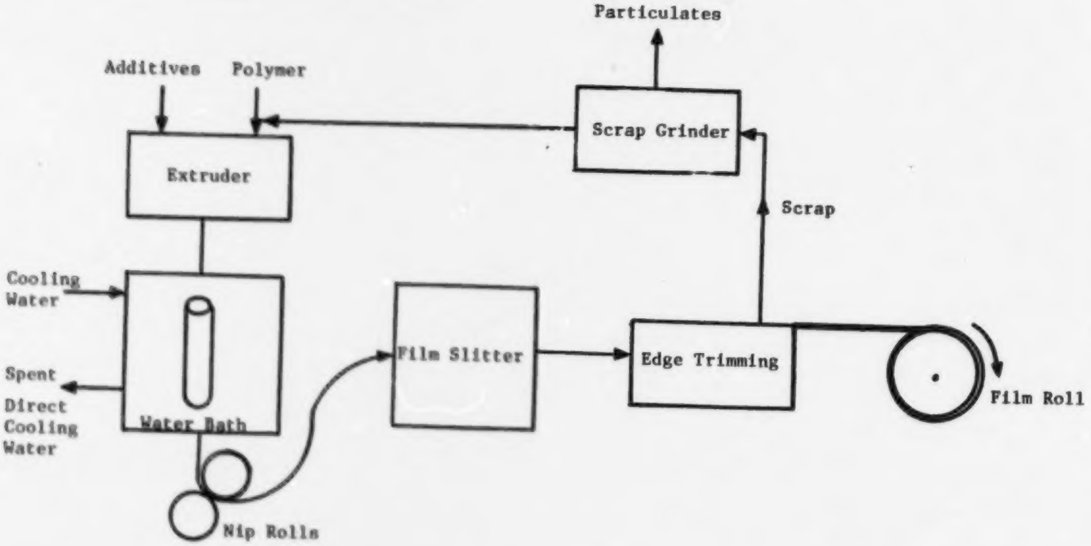

Particulates
Additives
Polymer
Scrap Grinder
Extruder
Scrap
Cooling Water
Spent Direct Cooling Water
Water Bath
Film Slitter
Edge Trimming
Film Roll
Nip Rolls

Figure 8. Chilled film casting.

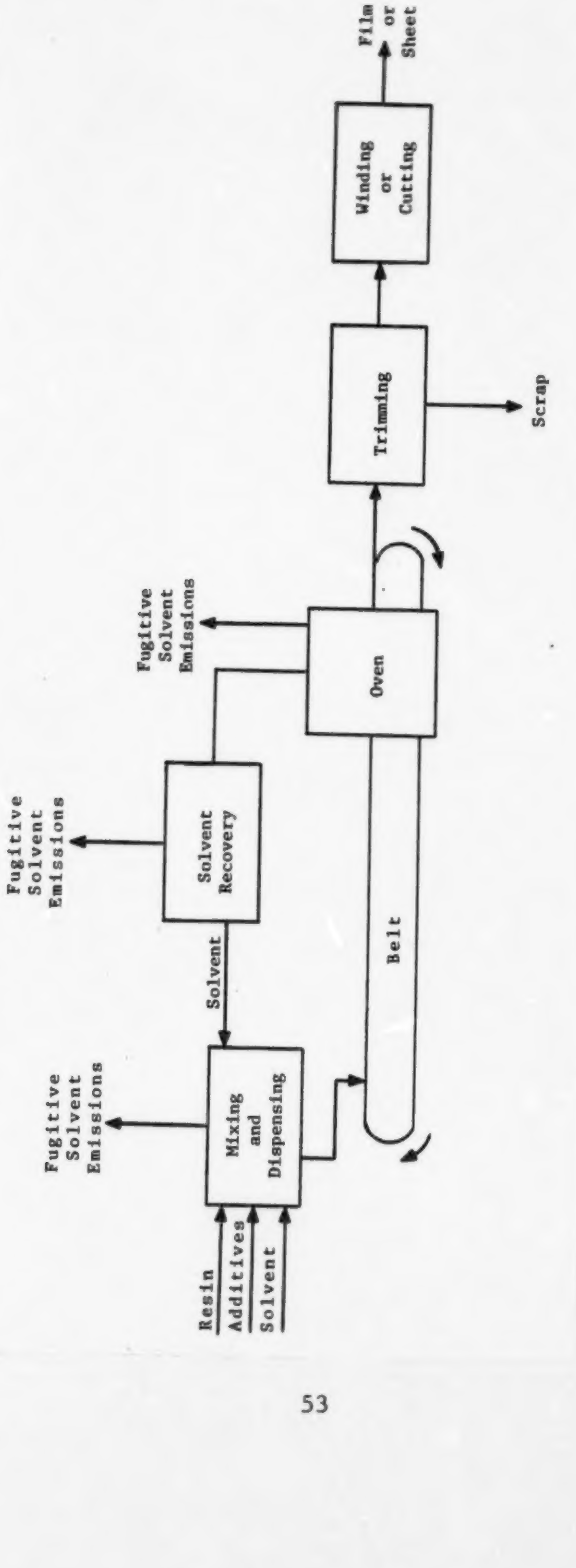

Resin
Additives
Solvent
Fugitive Solvent Emissions
Mixing and Dispensing
Solvent
Fugitive Solvent Emissions
Solvent Recovery
Belt
Fugitive Solvent Emissions
Oven
Trimming
Scrap
Winding or Cutting
Film or Sheet

Figure 9. Solvent casting.

for a .32 cm (.125 in.) sheet.[122] Sometimes oil or water baths are utilized to improve heat transfer for thicker sheets since they require very long oven curing times. In a few specialty applications, pressure is utilized to prevent bubbling in irregular or thick pieces.[122] Emissions may be liberated by the curing acrylic during the heating cycle.

Upon removal from the oven, the sheet is cooled in the cell, usually by ambient air, [122] after which it is stripped and trimmed to size. Often, cell cast acrylic sheet is paper or dip coated to provide a protective coating. In situations where special sheet surfaces are required, satin, mat, or ripple patterns are designed into the surface of the glass cell. A simplified block diagram of a cell casting process is shown in Figure 10.

A process similar to the cell casting of sheet is currently being developed for producing acrylic rods and tubes. Cylindrical glass tubes are used as the casting cells. To produce rods, acrylic is poured into the cells and they are heated vertically in a water bath. Rods are usually 0.91 to 45.7 cm (.357 to 18 in.) in diameter and up to 2.44 m (8 ft.) long.[29] To produce tubes, the cell is spun in the bath, forcing the acrylic to the sides and leaving a hollow center. Tubes usually have outer diameters of 3.81 to 60.96 cm (1.5 to 24 in.), with wall thicknesses between 0.32 to 1.27 cm (0.125 to 0.5 in.) and are up to 1.83 m (6 ft.) in length.[122] Cast acrylic rods and tubes usually need to be ground to form perfectly round products due to curing variations along the tube or rod. Grinding produces scrap acrylic which cannot be reused and must be disposed of as solid waste.

Continuous Casting processes produce thin continuous acrylic sheet. It is very similar to cell casting except that the liquid acrylic is cured between two highly polished moving stainless steel belts. The distance between the belts, which determines the thickness of the acrylic sheet, is controlled by flexible gaskets which are inserted between the belts. The continuous casting of sheet is generally limited to thin applications with widths up to 1.33 cm (.375 in.) [122] and provides more product uniformity than cell casting. The acrylic, trapped between the stainless belts, travels through the oven and air cooling stations. Emissions may be liberated during the heat curing of the acrylic. The edges are trimmed as necessary and the cast acrylic sheet is cut into flatsheet. A simplified block diagram of a continuous casting process is shown in Figure 11.

OPERATING PARAMETERS

Except for very specific process modifications, casting operations are performed at atmospheric pressure. The temperatures used in casting operations are highly dependent upon the polymer being processed and the product specifications. Casting operations which involve catalyzed polymer formulations usually do not require high temperatures to effect sufficient cures. Table 14 delineates the temperature requirements for each process and polymer formulation.

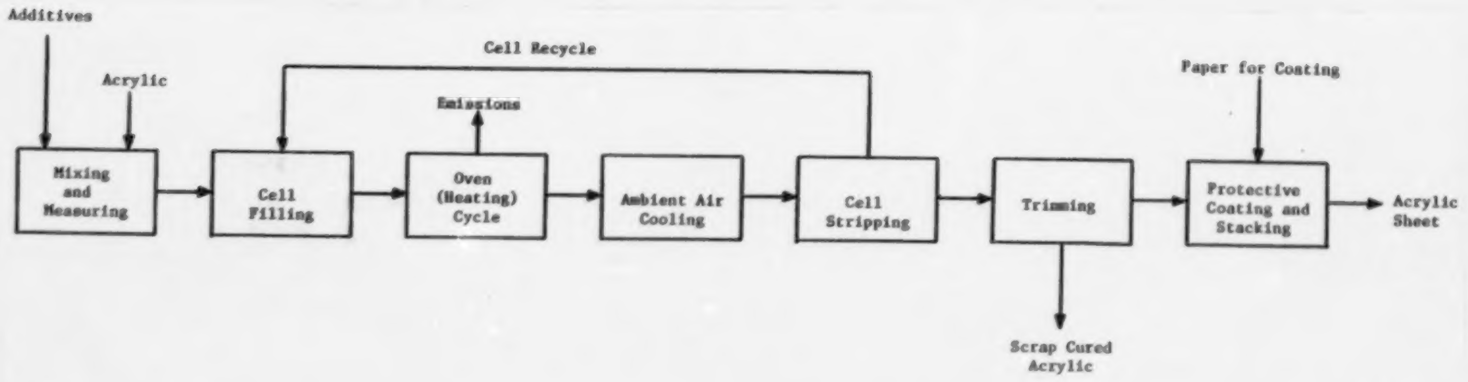

Additives
Acrylic
Mixing and Measuring
Cell Filling
Cell Recycle
Emissions
Oven (Heating) Cycle
Ambient Air Cooling
Cell Stripping
Trimming
Scrap Cured Acrylic
Paper for Coating
Protective Coating and Stacking
Acrylic Sheet

Figure 10. Cell casting.

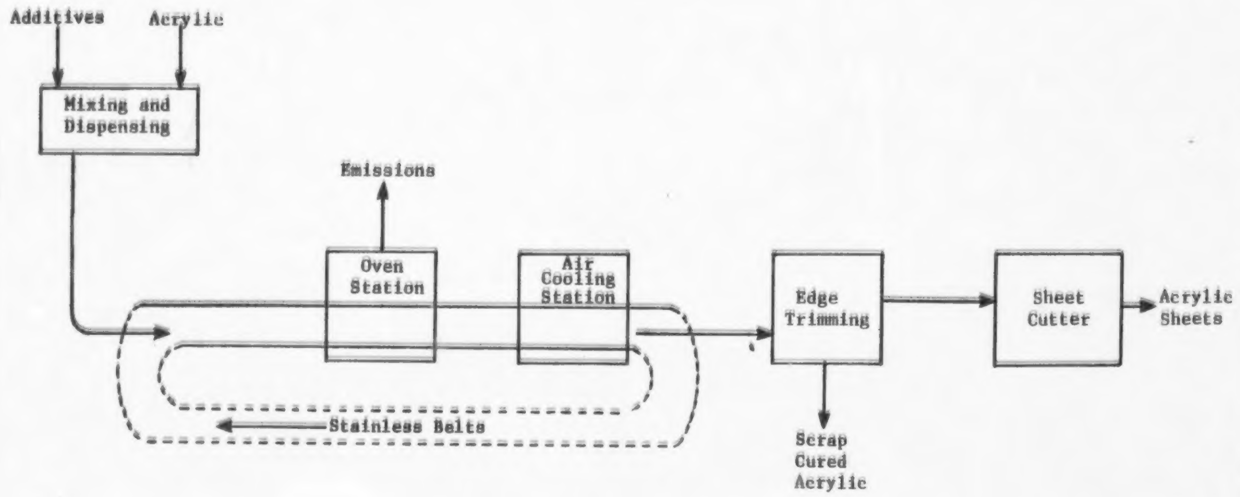

Additives
Acrylic
Mixing and Dispensing
Emissions
Oven Station
Air Cooling Station
Edge Trimming
Sheet Cutter
Acrylic Sheets
Stainless Belts
Scrap Cured Acrylic

Figure 11. Continuous casting.

TABLE 14. CASTING SYSTEM TEMPERATURE REQUIREMENTS

Casting Process	Polymer	Temperature Requirements (°C)
Pot Casting	Acrylic	90
	Allyl Resins	Catalyst - Temperature above 150
	Diallyl Phthalate	Catalyst - Temperature above 150
	Epoxy	Catalyst - Ambient Temperature Catalyst - 100
	Nylon	Catalyst - Ambient Temperature
	Phenolic	Catalyst - 160-188
	Polyester	Catalyst - Ambient Temperature
	Polyurethane	Catalyst - Low Temperature
Slush Casting	PVC Plastisol	177
Dip Casting	PVC Plastisol	177
Chilled Film Casting	Polyethylene	Extrusion Melt Temperature (200 - 230)
	Polypropylene	Extrusion Melt Temperature (230 - 260)
Solvent Casting	PVC Organosol	Above Solvent Evaporation Temperature
Cell Casting	Acrylic	45 - 90
Continuous Casting	Acrylic	45 - 90

Source: *Modern Plastics Encyclopedia*, 1981-1982.

WASTE STREAMS AND EMISSIONS

Casting operations produce air emissions, wastewater, and solid waste. Table 15 presents a summary of the point source emissions from casting operations. Emissions and wastes are discussed in more detail in the text below. Waste streams and emissions for major plastics additives used in casting are presented in more detail in the Industry Description section of this document.

Air Emissions - Fine particulates may be generated during the handling of the polymer, additives, and fillers prior to and during processing. Particulates are emitted during storage, blending, mixing, dispensing, and grinding operations. They can also be generated during the mixing and dispensing operations of pot casting and the scrap grinding operations of chilled film casting.

VOC emissions may occur during curing and/or heating of cast products. These emissions can be liberated from the curing of pot cast items, during the heating operation in cell and continuous casting, and during the heat fusion of PVC polymers in slush and dip casting. These emissions may contain volatilized monomers, plasticizers, cure reaction by products, or decomposition products. Decomposition products occur when excess heat causes the polymer to decompose. Table 16 presents those decomposition products which may be formed during casting. Emissions from the heat fusion of PVC polymers in slush and dip casting consist mostly of distilled plasticizers which are usually handled by oil or gas-fired afterburners.[129] Such emissions can be decreased by carefully choosing formulations which do not contain compounds which are volatile at the processing temperature.

Fugitive solvent emissions occur during the solvent casting process as the solvent-polymer formulation is mixed and dispensed and during solvent evaporation and recovery. These emissions contain vaporized solvents such as naphtha, diisobutyl ketone, or isophorone.[129]

Wastewater - Spent cooling water is produced by the direct contact cooling of cast products. Direct contact cooling is used during slush and dip casting operations and some pot casting operations. During tubular water bath casting, spent cooling water is produced by the film quench operation. Literature data were not found for this emission source; however, direct contact cooling water could potentially contain small amounts of fine plastic and filler particles as well as traces of plasticizers, catalysts, and other additives.

Solid Waste - Plastic scrap is produced by product trimming operations. In pot casting, thermoplastic scrap can be ground and used in low specification castings. Scrap thermoset can occasionally be ground and used as filler; however, it usually must be disposed of as scrap. Chilled film casting scrap is usually ground and recycled to the extruder feed in the appropriate ratios. The trimming of solvent cast film can sometimes be ground and reused in organosol formulation. Scrap cured acrylic from cell and continous casting operations usually cannot be recycled to the same film and sheet operations and must be disposed of as scrap. No problems should be presented by the disposal of such scrap since plastic scrap is characteristically inert.

TABLE 15. CASTING POINT SOURCE EMISSIONS

	Air Emissions								Wastewater				Solid Waste			
	Particulates			Volatiles												
	Polymer	Additives	Fillers	Monomer	Plasticizer	Cure By-Products	Decomposition Products	Solvent	Polymer	Plasticizer	Additives	Fillers	Polymer	Plasticizer	Additives	Fillers
Storage, Mixing, Dispensing, Trimming, & Grinding	X	X	X										X	X	X	X
Curing				X	X	X	X									
Solvent Casting								X								
Cooling									X	X	X	X				

TABLE 16. DECOMPOSITION PRODUCTS

Polymer	Highest Processing Temperature (°C)†	Decomposition Temperature (°C)§	Decomposition Products
Acrylic	90	320	*
Allyl Resins	150	225	*
Diallyl Phthalate	150	225	*
Epoxy	100	200	*
Nylon	310	300	CO_2, CO, NH_3 H_2O
Phenolic	188	300	*
Polyester	145	272	*
Polyethylene	230	100	Ketone carbonyl groups form due to oxidation
Polypropylene	260	300	*
Polyurethane	66	300	*,#
PVC	177	100	HCl

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*Decomposition products are not formed at or near the temperature reached during casting operations.

†This is the highest possible temperature reached by the normal casting of all formulations of the resin listed.

§This is the lowest temperature at which decomposition products begin to form.

#The presence of humidity at processing temperatures may cause hydrolysis of the urethane functional groups.

Contaminated plastisol waste from slush and dip casting operations cannot be reused and must also be discarded. Plastisol wastes contain large quantities of plasticizers. Scrap plastisol may or may not present a disposal hazard depending upon the plasticizer used and its concentration and extractability from the polymer.

WORKER DISTRIBUTION AND EXPOSURE

The six major plastics casting operations discussed in this section pose different manpower requirements. Worker distribution depends primarily on the operation's complexity and degree of automation. We have estimated worker distribution for each operation by correlating major equipment manhour requirements with the process flow diagrams shown in Figures 6 through 11. Worker distribution estimates are shown in Table 17.

Employees performing casting operations may be exposed to a variety of chemical substances and physical agents, depending on the plastics and additives handled, casting operation type, and degree of process automation. The most likely sources of overexposure are fugitive dust emissions from mixing, dispensing, trimming and cutting operations and volatile fugitive emissions from oven curing and solvent casting operations.

Major exposure substances and agents which may be present in casting operations are summarized in Table 18. Available toxicity information is summarized in Appendix C of this document and discussed in detail in Chapter 10, IPPEU and Chapter 10b, IPPEU.

TABLE 17. ESTIMATED WORKER DISTRIBUTION IN PLASTICS CASTING OPERATIONS

Operation	Unit	Workers/Unit/8-Hour Shift
Pot Casting	Mixing	0.5
	Molding machine	0.5
	Ejecting (if manual)	0.25
	Trimming	0.25
Slush/Dip Casting	Molding	0.5
Chilled Film Casting	Extrusion	0.5
	Chill rolling	0.5
	Trimming	0.25
	Grinding	0.25
Solvent Casting	Mixing/dispensing	0.5
	Film/sheet production	0.5
	Trimming	0.25
Cell Casting	Mixing	0.5
	Cell filling	0.5
	Cell stripping (if manual)	0.25
	Trimming	0.25
Continuous Casting	Mixing	0.5
	Belt filling	0.5
	Trimming	0.25

TABLE 18. CASTING EMISSIONS AND RELEASE POINT ESTIMATION

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Storage, mixing, trimming	Fugitives	Polymer Particulates - nuisance dust
		[1]Flame Retardants - alumina trihydrate
		- chlorinated paraffin wax
		[1]Heat Stabilizers - Ba/Cd stearate
		- Ca/Zn stearate
		[1]Plasticizers - di-n-octyl phthalate
		- diisooctyl phthalate
		- diisodecyl phthalate
		[1]Reinforcing Agents - glass fibers
		- asbestos
		- silica
		[1]Fillers - Ca carbonate
		- kaolin
		- diatomaceous earth
		- marble dust
		- iron filings
		- plaster
		- talc (no asbestos)
		- vermiculite
		- wood dust (soft)
		[1]Mold Release Agents - fluorocarbon spray
		- stearic acid
		- polyvinyl alcohol
		- silicone
		- vegetable oil
		- lecithin
	Mixing machines materials handling	Noise

(continued)

TABLE 18 (continued)

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Curing	Fugitives	[2]Residual Monomer - methyl methacrylate - epichlorohydrin - bisphenol-A - phenol - formaldehyde - trioxane - ethylene oxide - caprolactam - hexamethylendiamine - adipic acid - ethylene glycol - terephthalic acid - dimethyl terephthalate - 1,4-butanediol - 1,3-butadiene - ethylene - 1-butene - 1-hexene - 1-octene - vinyl acetate - propylene - heptane - styrene - vinyl chloride Plasticizer - di-n-octyl phthalate - diisoctyl phthalate - diisodecyl phthalate Cure By-Products [3]Solvent - isophorone - diisobutyl ketone - VM&P naphtha

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[1] Specific additives listed are those documented in the literature. Many other additives may be used, depending on product formulation specifications.

[2] Primary monomers used to produce the plastics typically formed via casting. Other monomers or comonomers may also be present.

[3] Solvent casting only.

SECTION 4

COATING

FUNCTION

Polymeric coatings are applied to a wide variety of substrates in order to provide certain properties for an intended product use. A choice of substrates accounts for the general integrity of the part whereas the plastic coating provides the finished product with special properties such as chemical resistance, toughness, humidity resistance, corrosion resistance, and electrical insulation.

Both thermosetting and thermoplastic resins may be used as coatings. The polymer coatings can be applied in the form of a melt, liquid, or finely divided powder. The plastics may be used as coatings for numerous substrates including other plastic objects, metal, wood, paper, fabric, leather, glass, concrete, and ceramics.[191]

There are a wide variety of processes which can be considered coating processes of one type or another. The coating processes which will be discussed in this section are:

- Plastisol Coating
  - Dip Coating
  - Spray Coating
- Powder Coating
  - Fluidized Bed Coating
  - Electrostatic Spray Coating
  - Electrostatic Bed Coating
- Spread or Knife Coating
- Extrusion Coating

Other processes which can be used as coating operations have been discussed in other sections of this document. The coating of wire and cable is discussed in the Extrusion section. Calender sheet and film coating are discussed in the Calendering section.

INPUT MATERIALS AND END PRODUCTS

Input materials to coating operations include thermoplastic and thermoset resins along with the additives required for their appropriate formulation. Commonly used polymers for coating include:

- Acrylic Resins
- Epoxy Resins
- Fluoroplastic
- Melamine and Urea Formaldehyde
- Nylons
- Polyester
- Low Density Polyethylene
- Polyethylene Terephthalate
- Polypropylene
- Polyurethane
- Polyvinyl Chloride

Depending upon the coating process which is to be employed, these coating resins are utilized in either a fine powder, plastic melt, or liquefied form.

Resin quality requirements are generally very demanding for use in coating operations. The reason for this is that coatings are thin layers of plastic which must be homogeneous and must uphold their integrity as a coating over many years, much use, and harsh conditions. Resins sold for coating operations are generally special coating formulas which require stringent quality control during manufacture. Coating resins therefore command higher prices than other general purpose resins.[191]

The properties of the resins are modified and enhanced by the use of additives such as colorants, plasticizers, UV absorbers, stabilizers, antioxidants, and hardeners. Additive formulations are uniquely determined in order to provide the properties desirable in the end product.

Typical products of coating operations include automotive parts, appliance parts, electrical supplies, furniture, and household gadgets. Table 19 presents a summary of the various coating operations, typical resin inputs to those operations, and typical end products. More detailed information on major plastics additives used in coating is presented in the Industry Description section of this document.

PROCESS DESCRIPTION

Coating operations will be discussed in this section in four general categories: Plastisol Coating, Powder Coating, Spread Coating, and Extrusion Coating. The waste streams which are shown in the process diagrams are discussed in more detail later in this section.

Plastisol Coating involves the use of a liquid plastisol which consists of fine particles of polyvinyl chloride (PVC) dispersed in plasticizers such as dioctyl phthalate. These plastisols are viscous at room temperature and can be made in a wide variety of colors. The nature of plastisols is such that the application of heat causes the resin and plasticizer to fuse into a homogeneous solid coating. Various plastisol coating methods exist with the most common ones being: dip coating and spray coating. Figure 12 presents a simplified block diagram of plastisol coating. Typical plastisol coated products include housewares and outdoor furniture.

TABLE 19. INPUT MATERIALS AND END PRODUCTS OF COATING OPERATIONS

Coating Operation	Input Materials	Typical End Products
PLASTISOL COATING Dip Coating	Polyvinyl Chloride with: Antioxidants Colorants Fillers Heat Stabilizers Plasticizers Solvents UV Stabilizers Viscosity Modifiers	Appliance coatings Battery clamps Dish drainer racks Electrical insulation Laundry baskets Outdoor furniture Pipes and fittings Electroplating racks Fabric gloves Automotive seat springs Lamp sockets Beverage container liners Medicine cabinet liners Refrigerator liners
	Epoxies Flame Retardants Hardener	Pipe coatings Food cans Drum coatings Aircraft and marine coatings Laboratory furniture Lawn chairs Appliances Hardware Automobile primers
	Fluoroplastics Polychlorotrifluoroethylene Colorants Polytetrafluoroethylene Solvent Dispersing Aids Surfactants Fluorinated Ethylene Propylene Nonionic and Anionic Dispersing Agents Polyethylene co Chlorotrifluoroethylene Polyethylene co Tetrafluoroethylene	Metallic surface coatings for food handling equipment, chemical mixing tank liners, valve and pump liners Glass coatings

(continued)

TABLE 19 (continued)

Coating Operation	Input Materials	Typical End Products
Spray Coating	Polyvinyl Chloride and Fluoroplastics with formulations similar to dip coating	Intricate designs and large parts
POWDER COATING Fluidized Bed Electrostatic Spray Electrostatic Bed	Acrylics with: Colorants Flow Control Agents Plasticizer Thixotropic Agents UV Absorbers	Automotive parts Appliance parts Kitchen accessories
	Epoxy with: Colorants Fillers Flow Control Agents Hardeners Reinforcers	Appliance parts Automotive parts Can and drum coatings Pipe coatings Metal furniture coatings Electrical insulation Exterior siding coating Hospital equipment Shelving Fire extinguishers
	Fluoroplastics	Appliance parts Automotive parts Food handling equipment Hardware Outdoor furniture
	Nylon 11, 12, and sometimes 6 Resin Modifiers: Colorants Dry Lubricant Waxes	Appliance parts Automotive parts Food handling equipment Hardware Outdoor furniture Industrial pipes and fittings Farm equipment
	Polyester Colorants Curing Agents	Appliance parts Automotive parts Building products Coil coatings Furniture
	Low Density Polyethylene	Marine containers and parts Pipe coatings

(continued)

TABLE 19 (continued)

Coating Operation	Input Materials	Typical End Products
SPREAD OR KNIFE COATING	Polypropylene UV Stabilizers Impact Modifiers	Hardware Machine hardware
	Polyvinyl Chloride	Automotive parts Furniture Machine parts Wire racks
	Low Density Polyethylene	Flexible coated paper and fabric for uses in packaging, outerware clothing, and upholstery textiles
	Polypropylene	
	Polyurethane	
	Polyvinyl Chloride (resin with particle size of 20-30 μm) Colorants Fillers Heat Stabilizer Plasticizer Surfactants UV Stabilizer Viscosity Modifiers	
	Melamine and Urea Formaldehyde Colorants Cure Catalyst Solvents Stabilizers	Coated paper and fabric Ceiling tile coating
EXTRUSION COATING	Fluoroplastics Polytetrafluoroethylene Colorants Lubricant	Liners
	Low Density Polyethylene Antiblocking Agents Antioxidants Antistatic Agents Colorants UV Stabilizers	Coatings for food applications such as milk cartons Multi-walled paper bags

(continued)

TABLE 19 (continued)

Coating Operation	Input Materials	Typical End Products
EXTRUSION COATING (Continued)	Polyethylene Terephthalate (PET)	Ovenable paper board Milk carton coating
	Polypropylene	
	Polyvinyl Chloride	Wallpaper Automotive and furniture fabrics Waterproof tarpaulin
	Nylon Plasticizers Resin Modifiers Waxes	Heat sealing surfaces for paper, glassine, metal foil, cellophane, and other plastics

Sources: Agranoff, Joan (ed). *Modern Plastics Encyclopedia, 1981-1982*, pp. 23, 40, 52.

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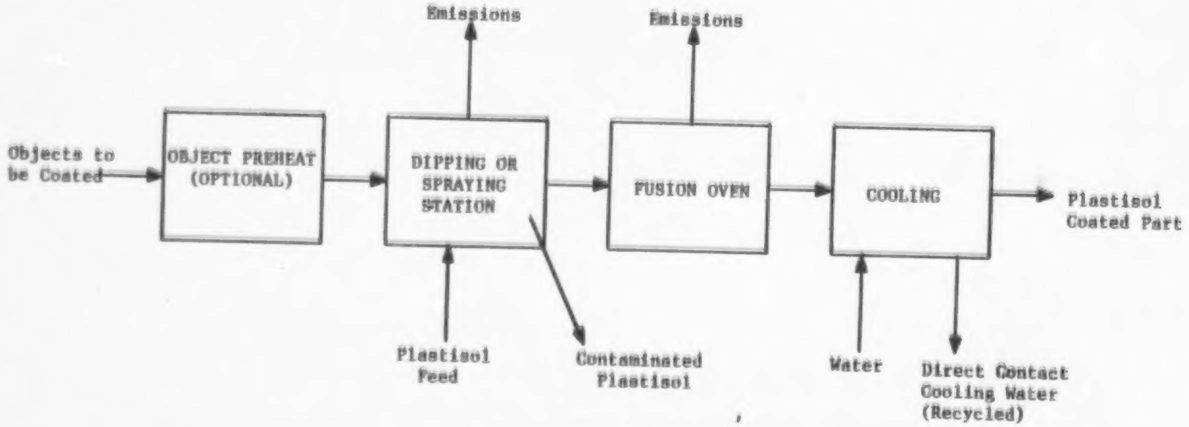
Objects to be Coated
OBJECT PREHEAT (OPTIONAL)
Emissions
DIPPING OR SPRAYING STATION
Plastisol Feed
Contaminated Plastisol
Emissions
FUSION OVEN
COOLING
Water
Direct Contact Cooling Water (Recycled)
Plastisol Coated Part

Figure 12. Plastisol coating.

A typical formulation for a vinyl solution useful for spray coating is given below:[158]

Material	Parts by Weight
PVC (resin)	15.0
Dioctyl Phthalate (plasticizer)	3.0
Methyl Isobutyl Ketone (solvent)	30.0
Toluene (solvent)	30.0
Propylene Oxide	0.2
Titanium Dioxide (colorant)	12.0
Phthalocyanine Green (colorant)	3.0

The dip coating process is very similar to the dip casting process which was discussed in the Casting section of this document. The difference lies in that in dip casting a mold is used whereas in dip coating the object to be coated serves as the mold. The plastisol is contained in a vat into which the object to be coated is dipped for three to five minutes.[15] Depending upon the nature of the object to be coated, the objects are sometimes preheated to assure sufficient polymer fusion. The dipped parts then pass through an oven at approximately 177°C (350°F) for five to 15 minutes to complete fusion.[15] The coated part is most often cooled with direct contact water sprays. The dip coating process can be performed manually or as a continuous mechanized process depending upon the manufacturers production requirement.

Spray coating involves spraying the plastisol onto the object surface. This is most often accomplished with a spray gun similar to that used for paint application. In some situations, the plastisol coating is applied with a brush. As in dip coating, the object to be coated can be preheated. Whether sprayed or brushed, the coated object must subsequently be heated in an oven to fuse the polymer coat.

Powder Coating involves the use of a homogeneous blend of thermoset or thermoplastic resin, pigments, fillers, and additives which is in the form of a dry, fine, flour-like substance. The powder for powder coating is produced by one of two methods. These methods are dry blend and melt mix. Dry blending involves mixing all the input materials as a batch process in a high intensity mixer or a ball mill at room temperature. Dry blending is used to prepare powders for use in the fluidized bed applications of powder coatings. The melt mix process is generally used for manufacturing thermoset powders. The input materials are premixed and then blended in the presence of heat (at approximately 30°C).[72] The molten resin is then cooled, flaked, pulverized, and sieved before use as a powder coating.

Powder coating will be discussed in this section in three basic categories: fluidized bed, electrostatic spray, and electrostatic bed. Figure 13 presents a block diagram of Powder Coating.

Fluidized bed coating involves creating a fluidized bed of thermoplastic or thermoset resin powder. This bed is created by the flow of air through a porous plate at the bottom of a tank. Resin placed above the plate becomes buoyant and acquires the apparent qualities of a fluid. Objects to be coated

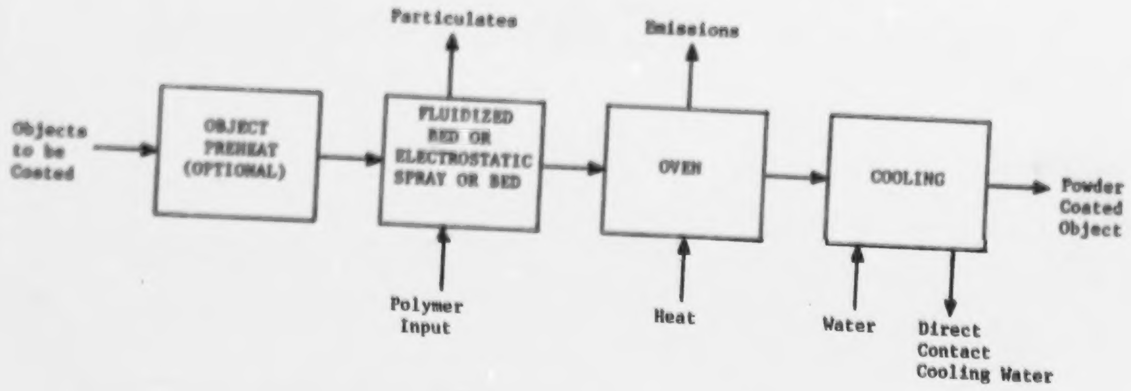
Objects to be Coated
OBJECT PREHEAT (OPTIONAL)
Particulates
FLUIDIZED BED OR ELECTROSTATIC SPRAY OR BED
Polymer Input
Emissions
OVEN
Heat
COOLING
Water
Direct Contact Cooling Water
Powder Coated Object

Figure 13. Powder coating.

(which are generally metal) are preheated to a temperature above the fusion temperature of the resin powder and are then dipped into the fluidized bed. When the resin particles touch the surface of the hot object they melt and fuse to the object surface forming a smooth finish. The coated part is then cooled by direct contact cooling water or air jets. Some products are dipped more than once to provide a thicker polymer coat. Masks are often used to cover sections of the part which should not be coated. Very little scrap plastic is created by fluidized bed coating since the polymer powder is efficiently reused during every dip.

A typical formulation for PVC powder coating is given below.[172]

Material	Parts by Weight
Polyvinyl Chloride Resin	100
n-Octyl n-Decyl Phthalate (plasticizer)	65
Epoxidized Soya Oil	5
$TiO_2/CaCO_3$ (pigment/extender)	25
Barium-Cadmium (stabilizer)	6
Organic Phosphite (stabilizer)	3
Dispersion-Grade PVC	5

Electrostatic spraying is performed by charging the polymer powder particles either positively or negatively so that they are attracted to a grounded or oppositely charged object. The powder is fed to the spray gun from the powder reservoir which is usually a fluidized bed or a mechanically agitated hopper. The powder is usually fed by means of a venturi air pump. The powder/air mixture is charged by an electrode close to the gun exit. The object to be coated either remains stationary in the path of the spray cloud (batch process) or it moves across the spray cloud (continuous process). The spraying is performed in an enclosed area allowing the powder to be collected and recycled by way of a cyclone followed by a bag collector.

The electrostatic bed process is a combination of the fluidized bed and electrostatic spray methods. A current of air passes upward through a fluidized bed and suspends the powder. Electrodes which are located in the porous plate at the bottom of the tank transfer a charge to the powder particles. The cold grounded object which is to be coated is passed over the bed. The electrostatic attraction of the powder to the object causes the powder to coat the surface of the object.

Knife or Spread Coating utilizes a long blade or knife to spread the polymer coating on the substrate. Figure 14 presents a block diagram and schematic of knife or spread coating. The substrate to be coated is moved by a set of rollers under a long blade or knife. Plastisols or molten thermoplastic are placed on the material just in front of the knife. The coating thickness is regulated by the distance between the knife and the substrate and the speed at which the substrate is drawn. The coated sheet then passes through an oven where the plastisol fuses into a homogeneous coating. Thermoplastics such as low density polyethylene, polyvinyl chloride, and polypropylene are used as spread coatings on flexible materials such as plastic or fabric. In all but specialty applications, knife coating has been replaced by extrusion coating.

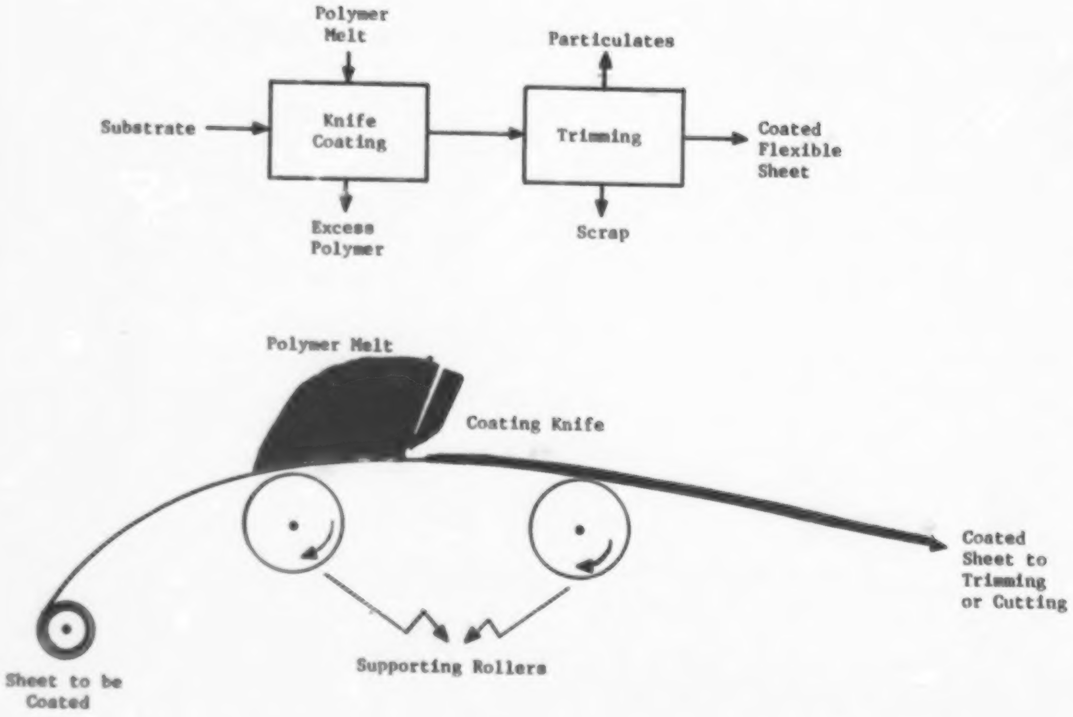
Polymer Melt
Substrate
Knife Coating
Excess Polymer
Particulates
Trimming
Scrap
Coated Flexible Sheet
Polymer Melt
Coating Knife
Coated Sheet to Trimming or Cutting
Sheet to be Coated
Supporting Rollers

Figure 14. Knife or spread coating.

Extrusion Coating involves the extrusion of a thin layer of polymer onto a moving substrate which is generally either a paper web, plastic sheet, or paper sheet. Figure 15 presents a block diagram of the extrusion coating process. The extrusion process used in extrusion coating is identical to that used for the extrusion of profile and sheet as described in Section 6. The processes differ in that at the extrusion die location, the plastic film is applied to a substrate. The coated substrate then passes between a chill roll and a nip roll. The water cooled chill roll removes heat from the molten polymer whereas the nip roll applies force to keep the two layers together until the polymer cools and the coating and substrate are bonded together. The coated product is then trimmed and cut according to product requirements. Two extruders can be used to perform two-sided coating on substrates. Polymers such as low density polyethylene, polypropylene, and polyethylene terephthalate are used in extrusion coating processes to produce coatings typically used in food packaging applications.

OPERATING PARAMETERS

Coating operations are performed at ambient pressures. The temperatures used during coating operations are highly dependent upon the polymer being processed and the specifications of the product. Plastisol coated products are generally heated to around 177°C (350°F) in order to fuse the polymer coating.[10] The temperatures used during powder coating are specific for each polymer used and are generally around the polymer fusion temperature. The temperatures used during spread coating and extrusion coating are very similar to those used for the regular-melt extrusion of each polymer.

WASTE STREAMS AND EMISSIONS

Coating operations produce air emissions, wastewater, and solid waste. Table 20 presents a summary of the point source emissions from coating operations. Emissions and wastes are discussed in more detail in the text below. The major plastics additives used in coating are presented in more detail in the Industry Description section of this document.

Air Emissions - Coating operations generate both particulate and volatile air emissions. Particulate emissions which contain fine particles of resin, plasticizer, and other additives can be released during powder coating. Particulates are released during extrusion hopper loading in extrusion coating and are produced by the trimming of spread and extrusion coated products. Such particulates contain particles of resin, plasticizer, and other additives. Control technologies used to control particulates include baghouse technology and wet scrubbing.

All coating operations have the potential to produce volatile emissions. Plastisol coating generates volatile emissions during the heating of the dipped or sprayed objects. When the objects are preheated prior to coating, volatile emissions can also occur during the dipping or spraying. Similarly, volatile emissions are released during the powder coating process from the post-coating oven. During extrusion coating, volatile emissions are released from vents in the extruder barrel as well as at the extruder die. Volatile emissions generated during coating consist of volatilized resin, plasticizer,

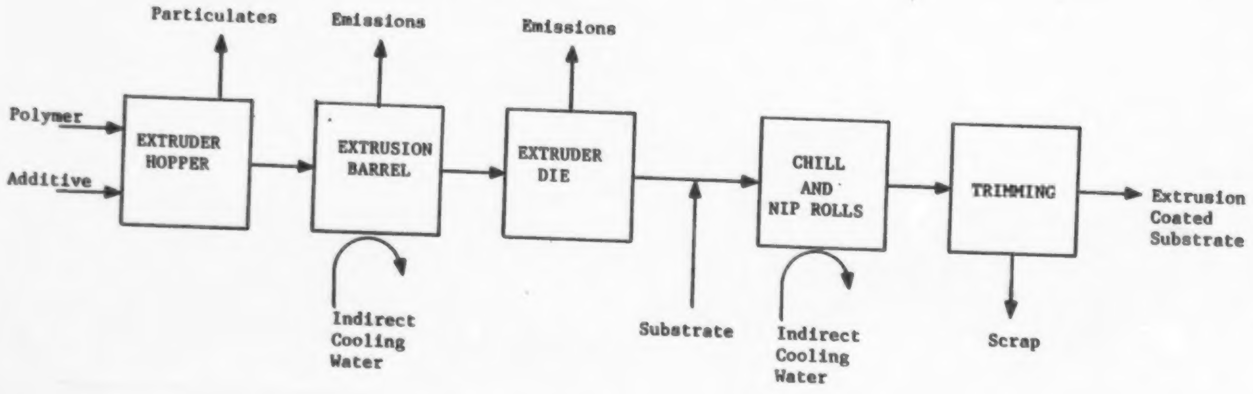
Particulates
Emissions
Emissions
Polymer
Additive
EXTRUDER HOPPER
EXTRUSION BARREL
EXTRUDER DIE
CHILL AND NIP ROLLS
TRIMMING
Extrusion Coated Substrate
Indirect Cooling Water
Substrate
Indirect Cooling Water
Scrap

Figure 15. Extrusion coating.

TABLE 20. COATING OPERATIONS POINT SOURCE EMISSIONS

	AIR EMISSIONS						WASTEWATER			SOLID WASTE		
	Particulates		Volatiles									
	Resin	Additives	Resin	Plasticizers	Additives	Decomposition Products	Resin	Plasticizers	Other Additives	Resin	Plasticizers	Additives
PLASTISOL COATING												
Dip Coating			X	X	X	X	X	X	X	X	X	X
Spray Coating			X	X	X	X	X	X	X	X	X	X
SPREAD COATING	X	X								X	X	X
POWDER COATING												
Fluidized Bed	X	X	X	X	X	X	X	X	X			
Electrostatic Spray	X	X	X	X	X	X	X	X	X			
Electrostatic Bed	X	X	X	X	X	X	X	X	X			
EXTRUSION COATING	X	X	X	X	X	X				X	X	X

other additives, and decomposition products. Decomposition products occur when the processing temperature exceeds that temperature at which decomposition occurs in the polymer. Decomposition products which are generated during coating operations are summarized in Table 21.

Wastewater - The use of direct contact cooling water to cool newly coated parts can result in the production of wastewater. Direct contact cooling occurs in both plastisol coating and powder coating. In most applications, the cooling water will be recycled, thereby greatly reducing the amount of wastewater which is actually produced. Wastewater produced in this manner may contain particles of resin, plasticizers, and other additives.

Solid Waste - Coating operations produce solid waste during trimming operations in knife and extrusion coating as well as due to the disposal of contaminated plastisol in plastisol coating operations and the dripping of excess polymer in knife coating operations. Solid waste from all of these operations cannot be recycled to the polymer feed and must be disposed of as a solid waste. Most of these wastes consist of primarily inert plastic containing small quantities of plasticizer and additives, and therefore, their disposal should pose no problems.

However, the contaminated plastisol scrap from plastisol coating operations may pose a disposal problem due to the high quantities of plasticizers which it contains. The most commonly used plasticizer, di-(2-ethylhexyl) phthalate (DEHP) is currently suspect as a carcinogen as a result of test data which indicates that it may cause cancer in rats.[160] The reliability of this test data is being questioned, and, as a result, scrap plastisol may or may not present a disposal hazard.

WORKER DISTRIBUTION AND EXPOSURE

Worker distribution in plastic coating operations is highly variable. Employee responsibilities may range from manual coating application to operation of a fully automated fluidized bed coating process. Because little data are reported in the literature regarding actual worker distribution in coating operations, we have estimated distribution using factors based on major equipment manhour requirements (see Figures 12 through 15). Estimates for each coating operation discussed in this section are shown in Table 22.

Potential for employee overexposure to harmful chemical substances and physical agents increases in coating operations requiring greater manual control of process units (e.g. plastisol or powder spray coating). However, little data exist in the literature from which employee exposure potential may be estimated. One source gives a range for hydrocarbon emissions from PVC coating operations: 35-75 g/kg product. Major contaminants which could be present in the workplace are summarized in Table 23. Toxicity information for these contaminants are summarized in Appendix C and discussed in detail in IPPEU Chapters 10 and 10b.

TABLE 21. DECOMPOSITION PRODUCTS

Polymer	Highest Processing Temperature (°C)†	Decomposition Temperature (°C)§	Decomposition Products
Acrylic Resins	230	320	*
Epoxy Resins	100	200	*
Fluoroplastic	330	300	HF
Melamine and Urea Formaldehyde	170	182	*
Nylons	310	300	CO_2, CO, NH_3, H_2O
Polyester	260	272	*
Low Density Polyethylene	230	100	Ketone carbonyl groups form due to oxidation
Polyethylene Terephthalate	300	300	Acetaldehyde
Polypropylene	230	300	*
Polyvinyl Chloride	210	100	HCl

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*Decomposition products are not formed at or near the temperature reached during coating operations.

†This is the highest possible temperature reached by normal coating operations with all formulations of the polymer listed.

§This is the lowest temperature at which decomposition products begin to form.

TABLE 22. ESTIMATED WORKER DISTRIBUTION IN PLASTIC COATING OPERATIONS

Operation	Unit	Workers/Unit/8-hour Shift
Plastisol Coating:		
Dip Process	Coating Line	0.5
Spray Process	Spray Gun Manual Applicator	1.0
Powder Coating:		
Dry/Fluidized Bed	Batch Mixer	1.0
	Fluidized Bed	0.5
Molten/Fluidized Bed	Batch Mixer	1.0
	Grinder	0.25
	Screens	0.25
	Fluidized Bed	0.5
Dry/Electrostatic Spray	Batch Mixer	1.0
	Spray Gun	1.0
Molten/Electrostatic Spray	Batch Mixer	1.0
	Grinder	0.25
	Screens	0.25
	Spray Gun	1.0
Dry/Electrostatic Bed	Batch Mixer	1.0
	Electrostatic Bed	0.5
Molten/Electrostatic Bed	Batch Mixer	1.0
	Grinder	0.25
	Screens	0.25
	Electrostatic Bed	0.5
Spread Coating:		
Dry Mix	Batch Mixer	1.0
	Knife Spreader	0.5
Molten Mix	Batch Mixer	1.0
	Grinder	0.25
	Screens	0.25
	Knife Spreader	0.5

(continued)

TABLE 22 (continued)

Operation	Unit	Workers/Unit/8-hour Shift
Extrusion Coating:		
Dry Mix	Batch Mixer	1.0
	Extrusion	0.5
	Trimming	0.25
Molten Mix	Batch Mixer	1.0
	Grinder	0.25
	Screens	0.25
	Extrusion	0.5
	Trimming	0.25

TABLE 23. PLASTIC COATING EMISSIONS AND RELEASE POINT ESTIMATION

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Plastisol Coating (Dip and Spray)	Fugitives (from curing ovens)	[1]Volatile polymer: - polyvinyl chloride - epoxy resin - fluoroplastics
		[2]Volatile Additives: Antioxidants - BHT - trisoronyl phosphite Colorants - carbon black - titanium dioxide - Cd sulfoselenide - phthalocyanines Flame Retardants - antimony oxide - alumina trihydrate - chlorinated paraffin wax Heat Stabilizers - tribasic lead sulfate - Ba/Cd stearate - Ca/Zn stearate UV Stabilizers - 2-hydroxy-4 octyl-benzophenone - dioctyl phthalate - diisooctyl phthalate - diisodecyl phthalate - tricresyl phosphate - di-(2-ethylhexyl) phthalate Reinforcers - silica Decomposition Products: - HF (fluoroplastics) - HCl (polyvinyl chloride)

(continued)

TABLE 23 (continued)

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Plastisol Coating (Continued)	Mixing, Grinding, Trimming, Materials Handling	Noise
Powder Coating (all types)	Fugitives (from coating)	[1]Polymer Particulates: - acrylics - epoxies - fluoroplastics - polyamides - polyesters - low density polyethylene [2]Additive Particulates - see additive list for plastisol coating.
	Fugitives (from curing ovens)	[1]Volatile Polymer [2]Volatile Additives Decomposition Products: - HF (fluoroplastics) - ketone carbonyls (polyethylene) - CO, NH_3, CO_2 (polyamides)
	Mixing, Materials Handling, Conveyor Rollers	Noise
Extrusion Coating	Extruder Barrel Vent	[1]Polymer Particulates - fluoroplastics - low density polyethylene - polyethylene terephthalate - polypropylene - polyamides - polyvinyl chloride

(continued)

TABLE 23 (continued)

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Extrusion Coating (Continued)		[2]Additive Particulates - see additive list for plastisol coating.
	Extruder Barrel Vent, Extruder Die, Fugitives (from coated sheet)	[1]Volatile Polymer [2]Volatile Additives Decomposition Products - HF (fluoroplastics) - ketone carbonyls (polyethylene) - acetaldehyde (polyethylene terephthalate) - HCl (polyvinyl chloride)
	Grinding/Trimming/Cutting	[1]Polymer Particulates Noise

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[1] Primary polymers used in plastic coating. Other polymers may be used for special applications.

[2] Specific additives listed are those documented in the literature. Many other additives may be used, depending on product coating formulations.

SECTION 5

COMPOUNDING

FUNCTION

Polymer compounding refers to the mixing of additives and specialty chemicals with a raw polymer before, during, or after polymer production and prior to or during processing to make the plastic applicable to its intended use. This step imparts physical and chemical properties which the polymer does not exhibit alone, reduces the cost of finished products, and/or increases the ease of production and processing. Since different raw polymers have widely different characteristics, formulations are tailor-made to meet the needs of the particular polymer and its application. Virtually all polymers require some formulation prior to processing.

Compounding may occur during either polymer production or processing. The decision of when to incorporate additives in the polymer is production and process specific. It is dependent upon the polymer properties, its means of production, and the method of processing. In actuality, a fine line exists between producing and processing polymers. In some situations, the polymer is produced, compounded, and processed at one location. In the majority of cases the polymer is sold to the processor uncompounded, partially compounded, or totally compounded for a specific application. The processor then completes compounding as necessary and begins processing. The processing steps which follow compounding operations are described in the remaining sections of this document.

A wide variety of techniques for compounding are used by the plastics and resins industry. These include:

- dry solids mixing,
- extrusion and other fluxed melt methods,
- liquid and paste mixing, and
- motionless mixing.

These methods are described in detail in the process description of this section.

INPUT MATERIALS AND END PRODUCTS

The input materials to the formulation processes are resins produced by the plastics and resins industry and additives or specialty chemicals used to make the polymer suitable for its end use. The wide range of additives used in polymer formulation originate from organic chemical producers, plastics and resins manufacturers, mining and minerals industries, and a host of other producers. There are literally thousands of possible formulations which require some type of compounding. A typical formulation for compounding by extrusion is presented in Section 6 of this document.

Additives function in two ways to modify polymer properties; by chemical and physical means. Chemical modifiers alter polymer properties through chemical reaction. These additives may react chemically with the polymer, or they may react preferentially with chemicals in the environment which would otherwise react with the polymer. Chemical modifiers include antioxidants, antistatics, coupling agents, flame retardants, foaming agents, heat stabilizers, and UV stabilizers. Thermosetting resins require curing agents and promoters for ease and quality of processing. Physical modifiers alter polymer properties through the additive's inherent characteristics. These modifiers include colorants, fillers and extenders, impact modifiers, lubricants, and plasticizers. The types of additives typically used in polymer formulation are described alphabetically in the following paragraphs. This listing is intended to highlight the various types of additives used in polymer processing. It is not comprehensive. More detailed information on major plastics additives is presented in the Industry Description section of this document. IPPEU Chapter 10b, Plastics Additives, contains a comprehensive evaluation of additives and their uses.

Activators, see Blowing Agents.

Accelerators, see Catalysts and Curing Agents.

Antiblocking Agents, also known as abherents, prevent adhesion of films to themselves. This term is specifically used for polyvinyl chloride (PVC), while the term slip agent is generally used for polyolefins. Silicate minerals and high melting waxes which migrate to the surface of the plastic are commonly used.

Antioxidants retard oxidative degradation of the plastic at processing temperatures and for extended life uses. The most commonly used antioxidants include alkylated phenols, amines, phosphates, and thio-compounds for polyolefins, polystyrene, and acrylonitrile-butadiene-styrene (ABS).

Antistatic Agents reduce the accumulation of electronic charge on the surface of polymers. These additives function either as lubricants to reduce friction and therefore reduce charge buildup or by providing a conductive path for dissipation of accumulated charge.

Blowing (Foaming) Agents produce large quantities of gases upon heating which form cellular plastics. These additives can be gases, solvents which volatize upon heating, or chemical agents which decompose to form gases. Activators may be used to promote gas formation. They are used for a wide variety of polymers. Cell stabilizers and nucleating agents control cell size and distribution in foamed plastics.

Buffers are compounds containing both weak acids and weak bases. The pH of solutions containing buffers changes only slightly upon addition of acid or alkali.

Catalysts affect the rate of chemical reactions without themselves being consumed or undergoing chemical change. The catalyst can be either an inorganic or organic compound or an element. The designation of catalyst is used rather loosely in plastics processing, since some compounds designated as catalysts are consumed by the reaction, for example peroxides. Because catalysts are not consumed in the reaction, catalyst neutralizers are sometimes added to deactivate or limit the catalyst's activity following processing and during product use.

Catalyst Neutralizers, see Catalyst.

Cell Stabilizers, see Blowing Agents.

Chain Transfer Agents react with a growing polymer molecule to remove its free radical site and terminate polymer growth. The chain transfer agent is then a free radical capable of initiating the growth of another polymer chain.

Coalescing Agents, see Solution Modifiers.

Colorants impart hue (shade), value (brightness), and chroma (strength of color) to plastics. They increase the aesthetic appeal of a product, and may enhance other properties including strength and UV stability. This broad classification includes dyes, organic and inorganic pigments, delusturants, pearlescents, and metallics.

Coupling Agents enhance polymer-mineral surface bonds and the ability of a composite to retain its original properties after prolonged exposure to moisture. Silane and titanate compounds are high volume chemicals in this class. They are most commonly used with fibrous glass reinforcers which often improve other physical properties of the plastic such as flexural and tensile strength. Further, the cost of the composite is frequently reduced due to the addition of glass filler.

Craze Resistant Agents reduce the tendency of a polymer to crack. These are commonly used in amino resins.

Crosslinking Agents form a bridge between individual polymer chains, changing a thermoplastic to a thermosetting resin. Divinylbenzene is commonly used with polystyrene, organic peroxides with polyethylene.

Cure Retardants reduce the cure rate for thermosetting resins. They are most commonly amines used in amino resins.

Curing Agents improve the curing of thermosetting resins upon exposure to heat. They commonly include peroxides, amines, and azo compounds with polyester, amino, and phenolic resins. Organotin and amine compounds are commonly used with polyurethanes.

Defoamers, Diluents, Dispersing Aids, and Emulsifiers, see Solution Modifiers.

Elastomers and Flexibilizers increase the pliability of polymers, and reduce their tendency to break.

Fillers and Extenders increase the bulkiness and decrease the total cost of plastic formulations. These compounds generally tend to reduce the desirable properties of the plastic, although some fillers are added to also reinforce, harden, insulate, and improve the appearance of the plastics they fill.

Flame Retardants act chemically or physically as insulators; by creating endothermic cooling reactions, by coating the plastic to exclude oxygen, or by influencing combustion through reaction with materials that have different physical properties. Antimony, halogen, boron, nitrogen, and phosphorus based compounds are most common. Smoke suppressants and self-extinguishing agents are also used to reduce the fire hazard of polymers.

Flow Control Agents either promote or inhibit the flow properties of thermosetting resins.

Fungicides, see Preservatives.

Hardeners can be either internal or external. These compounds improve the firmness and set of resins. See also Curing Agents.

Heat Stabilizers are primarily used in PVC and other vinyl formulations. These additives prevent the degradation of the plastic during process heating and for extended life uses. A variety of organic and organometallic compounds are used to react with chlorine radicals formed during heating and thus limit further degradation of the polymer.

Impact Modifiers decrease the plastic's tendency to break or crack upon impact. These additives include polymers such as acrylics and chlorinated polyethylene, and are primarily used in PVC formulations.

Initiators, see Catalysts and Curing Agents.

Inhibitors prevent the polymerization of resins during storage and blending.

Lubricants enhance resin processibility and appearance of the end product. Desirable properties for lubricants include compatibility with the resin, ease of mixing, and FDA approval (where applicable). The lubricant should not adversely affect the end product. Common lubricants include fatty acid esters, hydrocarbon oils and paraffin wax, and amides.

Mold Release Agents coat the mold to prevent sticking of newly formed parts and to reduce static buildup. These additives can be sprays, powders, or paint-on liquids. Silicone, fluorocarbons, mineral oil, waxes, fatty acids, mica, and talc are used as mold release agents.

Neutralizers, see Solution Modifiers.

Peroxide Decomposers, see Catalyst Neutralizers.

Plasticizers impart flexibility, resiliency, and melt flow to polymers. These additives act by reducing the intramolecular forces between polymer chains. Eighty percent of plasticizers are used in PVC formulation. The major chemical classes include phthalates, adipates, trimellitates, glycolates, epoxies, polyesters, and other fatty acid esters and organic phosphates.

Preservatives and Biocides inhibit biological degradation of polymers. This class of additives includes fungicides and bacteriostats.

Promoters, see Catalysts and Curing Agents.

Protective Colloids, see Solution Modifiers.

Reinforcing Agents impart tensile, flexural, and compressive strength to plastics. These reinforcers can be synthetic fibers, carbon fibers, glass fibers, asbestos, silica, or other combinations of materials. The most common reinforcers are glass fibers which are available in chemical and electrical grades to provide increased chemical resistance and electrical insulating properties, respectively, to the plastic.

Reodorants improve the olefactory appeal of polymers by masking their odor.

Sizing Agents are coatings which protect the polymer surface. Waxes are commonly used.

Slip Promoters provide surface lubrication during processing and use. They have minimal compatibility with the polymer, are added internally, and flow to the surface immediately following processing. Since compatiblity is minimal, slip promoters may exude from the product long before the end of its useful life. This term is commonly applied to abherents for polyolefins.

Solution Modifiers include a wide variety of chemicals used for plastisols, coatings, and latexes. These additives have a wide variety of uses, but are mainly incorporated for ease of handling and for application to the selected processing step.

Solvents, Surfactants and Suspension Aids, see Solution Modifiers.

Stabilizers include a wide variety of compounds which improve the stability of plastics during processing and use. See Antioxidants, Heat Stabilizers, and UV Stabilizers.

Thixotropic Agents are used for thermosetting resins to promote gelling upon standing, and liquefaction upon shaking.

UV Stabilizers function either to absorb ultraviolet radiation and reradiate it at a harmless wavelength or as quenchers which consume the free radicals generated by UV light. Benzotriazoles and benzophenones constitute the major compounds used as UV absorbers. Nickel compounds are commonly used as quenchers.

Viscosity Aids reduce or increase the viscosity of plastisols (PVC-plasticizer-solvent mixtures) either during normal processing or for plastisols which have been subjected to prolonged storage.

Table 24 details the additive classes used for each polymer application, and the techniques utilized in compounding. Many of the polymers listed do not include blending processes. In these cases, the processes used for compounding were not found in the literature sources cited. Many of these resins, particularly the thermosets, utilize batch mixing in large vats for compounding additives, others are mixed in holding tanks preceding polymerization. For more information on the particular chemical inputs to the various polymer processing steps, see the specific process description sections of this document.

PROCESS DESCRIPTION

Compounding of polymer resins can be performed by a variety of methods. The technique chosen is dependent upon the form of the resin available for compounding, the additives to be incorporated and their physical and chemical properties, and the requirements of the processing steps utilized to form the end product. Many operations require multistage blending, and multivariate combinations of the blending processes discussed below are possible. A typical compounding process involves adding the polymer and additives in appropriate proportions to the mixing vessel or hopper. The polymer is then preblended in the dry, paste, or liquid form to obtain a homogeneous mix of additives. Further blending is achieved through polymer melting and incorporation of additives into the polymer matrix. Finally, the polymer is discharged to pelletizers, dryers, or processing equipment. Loading and blending will be discussed in this process description. Drying, pelletizing, and processing are detailed in other sections.

Granulators are used to process scrap sprues, edge trim from film and sheet, runners and rejected parts for recycle into compounding or processing operations. Table 25 details information concerning the reprocessibility of plastics. Occasionally, granulators are used for coarse blending of agglomerates with the scrap. The granulator consists of a hopper and cutting chamber. The blades cut and mix the scrap plastic. Particulate formation is likely in these cutting operations. Solid waste is generated during screen cleaning.

Polymer blending operations cannot readily be categorized according to the physical state of the polymer and additive inputs. Many of the mixing designs discussed in this section can be used for dry solids, paste, or liquid mixing. The particular blending technique chosen is dependent upon polymer characteristics and subsequent processing needs. For this reason, the blenders and mixers discussed here are listed essentially in order of their sophistication and the degree of mixing achieved.

TABLE 24. INPUT MATERIALS AND PROCESSES IN COMPOUNDING

Polymer	Formulation	Process
Acrylic Resins	Antistatic Agents	Extrusion
	Blowing Agents	Dry Tumbler (such as Double Cone)
	Catalysts	
	Chain Transfer Agents	
	Colorants	
	Flame Retardants	
	Flow Control Agents	
	Impact Modifiers	
	Lubricants	
	Mold Release Agents	
	Plasticizers	
	Thixotropic Agents	
	UV Stabilizers	
Acrylonitrile-Butadiene-Styrene (ABS)	Activators	Banbury Mixers
	Antioxidants	Extruders (single and twin screw)
	Antistatic Agents	
	Blowing Agents	Two Roll Mills
	Colorants	Motionless Mixers
	Emulsifiers	
	Flame Retardants	
	Initiators	
	Lubricants	
	Reinforcing Agents	
	Stabilizers	
	Suspension Aids	
	Transfer Agents	
	UV Stabilizers	
Alkyd Resins	Accelerators	
	Catalysts	
	Colorants	
	Coupling Agents	
	Cure Agents	
	Drying Oils	
	Fillers	
	Flame Retardants	
	Flow Improvers	
	Impact Modifiers	
	Mold Release Agents	
	Plasticizers	
	Reinforcing Agents	
	Reodorants	
	Solvents	

(continued)

TABLE 24 (continued)

Polymer	Formulation	Process
Alkyd Resins (Cont.)	Stabilizers Thixotropes UV Stabilizers Viscosity Modifiers	
Amino Resins	Catalysts Catalyst Neutralizers Colorants Curing Agents Fillers Flow Control Agents Hardeners Lubricants Modifiers Mold Release Agents Plasticizers Reinforcing Agents Solvents Stabilizers	Banbury Mixers Ball Mills Granulators Sigma Blade Mixers Dry Tumbler Ribbon Blenders
Modified Polyphenylene Oxide and Polyphenylene Sulfide		
Polyphenylene Oxide	Blowing Agents Colorants Flame Retardants Polymeric Modifiers	
Polyphenylene Sulfides	Colorants Fillers Lubricants Mold Release Agents Reinforcing Agents UV Stabilizers Wetting Agents	Granulators Extruders Predry Paddle and Double Arm Mixers Banbury Mixers
Epoxy Resins	Accelerators Catalysts Colorants Coupling Agents Curing Agents Diluents Fillers	Paddle and Double Arm Mixers

(continued)

TABLE 24 (continued)

Polymer	Formulation	Process
Epoxy Resins (Cont.)	Flame Retardants	
	Flow Control Agents	
	Hardeners	
	Impact Modifiers	
	Lubricants	
	Mold Release Agents	
	Plasticizers	
	Reinforcing Agents	
	Stabilizers	
	UV Stabilizers	
	Viscosity Modifiers	
Fluoropolymers		
Polyvinylidene Fluoride	Activators	Two Roll Mills
	Blowing Agents	
	Colorants	
	Crosslinking Agents	
	Curing Agents	
	Fillers	
	Plasticizers	
	Reinforcing Agents	
Other Fluoropolymers	Catalysts	Granulators
	Colorants	Extruders
	Curing Agents	
	Dispersing Aid	
	Emulsifiers	
	Fillers	
	Initiators	
	Lubricants	
	Promoters	
	Reinforcing Agents	
	Solvent	
	Stabilizers	
	Surfactants	
Phenolics	Blowing Agents	Extruders
	Colorants	Granulators
	Catalysts	Ball Mills
	Coupling Agents	Ribbon Blenders
	Crosslinking Agents	Banbury Mixers
	Curing Agents	Sigma Blade Mixers
	Fillers	Two Roll Mills

(continued)

TABLE 24 (continued)

Polymer	Formulation	Process
Phenolics (Cont.)	Flow Improvers Inhibitors Lubricants Neutralizers Plasticizers Promoters Reinforcing Agents Reodorants	
Polyacetals	Antioxidants Blowing Agents Colorants Fillers Lubricants Reinforcing Agents Stabilizers UV Stabilizers	Extrusion
Polyamide Resins	Accelerators Activators Antioxidants Catalysts Colorants Flow Control Agents Fillers Heat Stabilizers Plasticizers Reinforcing Agents Slip Promoters UV Stabilizers	Extruders Granulators
Nylons	Antiblocking Agents Antioxidants Antistatic Agents Blowing Agents Colorants Fillers Flame Retardants Heat Stabilizers Lubricants Nucleating Agents Plasticizers Reinforcing Agents UV Stabilizers	Extruders

(continued)

TABLE 24 (continued)

Polymer	Formulation	Process
Polycarbonate	Antioxidants Blowing Agents Colorants Flame Retardants Lubricants Mold Release Agents Reinforcing Agents Stabilizers	Two Roll Mills Extruders Predry
Polyethylene		
High Density Polyethylene (HDPE)	Antiblocking Agents Antioxidants Blowing Agents Colorants Crosslinking Agents Fillers Flame Retardants Impact Modifiers Reinforcing Agents Stabilizers UV Stabilizers	Extruders (single and twin screw) Banbury Mixers Two Roll Mills Granulators Tumblers Intensive Vortical Action Mixers Motionless Mixers
Linear Low Density Polyethylene (LLDPE)	Acid Neutralizers Antiblocking Agents Antioxidants Antistatic Agents Colorants Metal Deactivators Reinforcing Agents Stabilizers UV Stabilizers	Single Screw Extruders Twin Screw Extruders Tumblers Banbury Mixers Granulators Two Roll Mills Intensive Vortical Action Mixers Motionless Mixers
Low Density Polyethylene (LDPE)	Antiblocking Agents Antioxidants Antistatic Agents Blowing Agents Colorants Crosslinking Agents Fillers Flame Retardants Impact Modifiers Peroxide Decomposers Reinforcing Agents UV Stabilizers	Extruders (single and twin screw) Two Roll Mills Granulators Tumblers Banbury Mixers Intensive Vortical Action Mixers Motionless Mixers

(continued)

TABLE 24 (continued)

Polymer	Formulation	Process
Polyethylene Terephthalate Polybutylene Terephthalate	Antioxidants Antistatics Colorants Fillers Flame Retardants Modifiers Reinforcing Agents	
Polypropylene	Antiblocking Agents Antioxidants Antistatic Agents Blowing Agents Colorants Fillers Flame Retardants Impact Modifiers Lubricants Plasticizers Reinforcing Agents Stabilizers UV Stabilizers	Intensive Vortical Action Blenders Extruders Motionless Mixers
Polystyrene	Antioxidants Antistatic Agents Blowing Agents Colorants Corrosion Inhibitors Fillers Flame Retardants Flow Improvers Impact Modifiers Inhibitors Lubricants Mixing Aids Mold Release Agents Reinforcing Agents Stabilizers UV Stabilizers	Extruders Banbury Mixers Motionless Mixers
Polyurethane	Antioxidants Blowing Agents Catalysts Cell Stabilizers Colorants Curing Agents	Generally mixed by batch in the feed tank

(continued)

TABLE 24 (continued)

Polymer	Formulation	Process
Polyurethane (Cont.)	Flame Retardants	
	Flow Controllers	
	Lubricants	
	Modifiers	
	Plasticizers	
	Promoters	
	Reinforcing Agents	
	Surfactants	
	UV Stabilizers	
Polyvinyl Acetate	Antioxidants	
	Coalescing Agents	
	Colorants	
	Crosslinking Agents	
	Defoamers	
	Extenders	
	Plasticizers	
	Preservatives	
	Reinforcing Agents	
	Solvents	
	Surfactants	
	Thickeners/Protective Colloids	
Polyvinyl Alcohol	Antiblocking Agents	Extruders
	Colorants	Grinders
	Extenders	Ball Mills
	Plasticizers	
Polyvinyl Chloride (PVC)	Antiblocking Agents	Two Roll Mills
	Antioxidants	Banbury Mixers
	Antistatic Agents	Tumbler Blenders
	Blowing Agents	Ribbon Blenders
	Colorants	Paddle and Double Arm Mixers
	Diluents	
	Fillers	Extruders
	Flame Retardants	Intensive Vortical Action Mixers
	Fungicides	
	Heat Stabilizers	
	Impact Modifiers	
	Lubricants	
	Plasticizers	
	Reinforcing Agents	
	Solvents	

(continued)

TABLE 24 (continued)

Polymer	Formulation	Process
Polyvinyl Chloride (PVC) (Cont.)	Surfactants UV Stabilizers Viscosity Depressants	
Polyvinylidene Chloride	Antioxidants Chelating Agents Colorants Heat Stabilizers Plasticizers UV Stabilizers	Paddle and Two Blade Mixers Extruders
Styrene Acrylonitrile (SAN)	Chain Transfer Agent Elastomers Emulsifier Fillers Initiator Lubricants Reinforcing Agents Suspending Agents UV Stabilizers	Extruders

Sources: Bikales, Norbert M. (ed). *Encyclopedia of Polymer Science and Technology*, (Vol:pp): 4:118-129, 6:316; 7:215; 10:749-757; 11:611; 13:422, 430; 14:118-129, 421-433; 15:649-662.

Gaylord, Norman G. (ed). *Encyclopedia of Polymer Science and Technology*, Vol. 2, pp. 32-39.

Grayson, Martin (ed). *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd Edition, (Vol:pp): 1:445-450, 436-441, 118-119; 2:448-454; 15:119-207; 16:465-467, 445-446, 414-417, 394-396; 17:405-410; 18:488, 802-805.

Reed, George V., "Improving PP with Phosphite Stabilizers," *Modern Plastics*, November 1979, p. 76.

Shreve, R. N. and J. A. Brink, Jr., *Chemical Process Industries*, 4th Edition, 1977, pp. 576-577, 584.

Standen, A. (ed). *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd Edition, (Vol:pp): 19:110; 21:269-275, 296-303, 390-302, 402-405.

TABLE 25. REPROCESSIBILITY OF PLASTICS

	Insignificant Change	Slight Degradation	Moderate Degradation	Significant Degradation	Useful Only as Fillers
Polyethylene	X				
Plasticized PVC		X			
Polystyrene	X				
Impact Polystyrene		X			
Polycarbonate			X		
Polypropylene		X			
Polymethyl Methacrylate		X			
ABS			X		
Nylon			X		
Unplasticized PVC				X	
Polyacetal				X	
Thermosets					X

Source: Beadle, John D. (ed). Plastics Forming, 1971, p. 158.

Loading and Preblending - This operation consists of a variety of processes which load the polymer and additives into the blender or hopper. Loading can be performed manually, with the formulation added quantitatively, or it can be done through a series of automatic weighing and feeding devices. Many of these are controlled through microprocessors which allow for flexibility in formulating. Conveyors, vacuum lines, and liquid pumps are used to transport and mix ingredients.

Predrying of polymer pellets is necessary for hygroscopic and moisture sensitive materials, particularly nylon and polycarbonate. This operation is generally performed using dehumidifying air which is continuously pumped through the process stream. The dry air is obtained by purging through a dessicant.

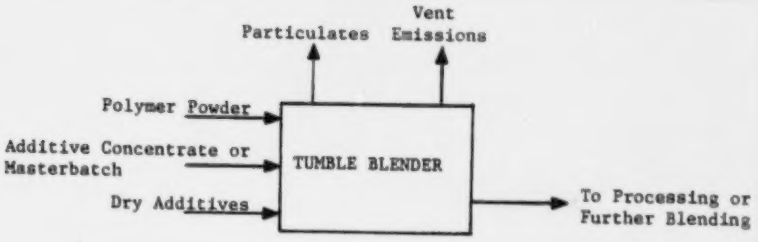
Loading, drying, and preblending operations can be a significant source of particulates. Good housekeeping procedures, filters, and screens can reduce some of these emissions. Volatile emissions are possible from low boiling additives. Solid wastes may be generated from screening operations.

Tumble Blenders - Commonly used for preblending because of their low cost and ease of operation, these mixers are suitable for solids of essentially the same size, and are available in a variety of shapes. These include horizontal and inclined cylinders, double cones, twin shells, and Y-shaped cones. These mixers rely upon the rotation of the mixer shell to disperse particles. Tumble blenders also include ball and pebble mills which hold high density balls or pebbles for breaking agglomerates as the exterior shell of the blender rotates. These mills produce powders with exact shades of color and can be used for resins available as both solids and liquids. They are heavily used in compounding amino resins.

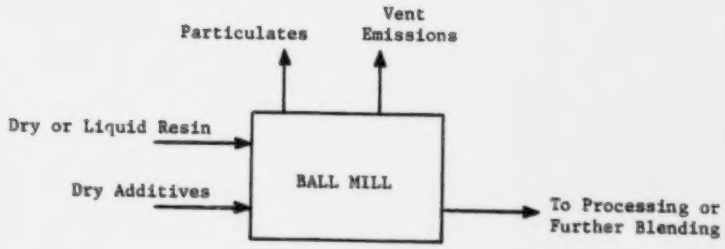
Tumble blenders generate particulate and volatile emissions. Particulates are possible, particularly in the loading and unloading of the resin and additives and from fugitive sources as the blending proceeds. Heat buildup during blending could be expected to volatilize low boiling additives and residual monomer, since jacketing of tumble blenders is difficult, thus, economically impractical. Figure 16 shows a block diagram of these blending processes.

Gravity Mixers - These dry solid mixers consist of a series of baffles or cascades designed to achieve optimum blending of the polymer resin and dry additives using the force of gravity. Centered screw/auger types lift the dry powders allowing for several passes through the cascades, and thus increasing the extent of mixing. A block diagram of these blenders is shown in Figure 16. Particulate emissions can be anticipated from loading and unloading of these mixers and from fugitive sources as they fall through the cascades.

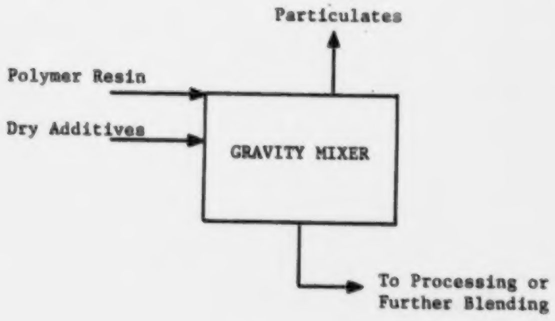
Conical Mixers with Orbiting Screw - These mixers are used for solid/solid blending and paste dispersion. The blender continually transfers material to different vertical planes, with the screw lifting and mixing radially around the cone-shaped bowl. This type of mixer is well suited for blending particles of widely differing shapes, sizes, and densities.


Particulates
Vent Emissions
Polymer Powder
Additive Concentrate or Masterbatch
Dry Additives
TUMBLE BLENDER
To Processing or Further Blending

TUMBLE BLENDERS


Particulates
Vent Emissions
Dry or Liquid Resin
Dry Additives
BALL MILL
To Processing or Further Blending

BALL MILLS


Particulates
Polymer Resin
Dry Additives
GRAVITY MIXER
To Processing or Further Blending

GRAVITY MIXERS

Figure 16,

Particulate emissions from loading and unloading operations along with venting of the blend are possible in this operation. A block diagram of this blender is shown in Figure 17.

Paddle and Double Arm Mixers - These blenders have either paddles attached to a centered axis or two blades which revolve in a trough. The blades of the double arm mixers can either overlap or rotate tangentially. The traditional s-shaped (sigma) blade is used in these operations along with other configurations. This provides intense shearing, stretching, kneading, and folding. A block diagram of paddle and double arm blenders is shown in Figure 17. These blenders are particularly suited to highly viscous blends such as heavy pastes, mastics, caulks, silicone elastomers, filled epoxies, rubbers, hot melts, bulk molding compounds, and highly filled materials.

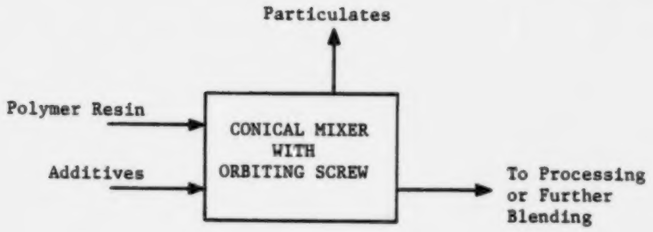
Both batch and continuous flow units are available with dust and vapor-tight designs. Particulate and volatile emissions of monomer, degraded polymers, and additives are possible with this type of blender.

Ribbon Blenders - These conical rotary containers have mounted arms supporting spiral ribbons, flights, helical screws, or paddles. An exterior set of ribbons move the material in one direction, while the interior blades move it in the opposite. Figure 18 depicts a block diagram of this mixer. This blender can be used for powders, pastes, or liquids and is heavily used in the blending of PVC.

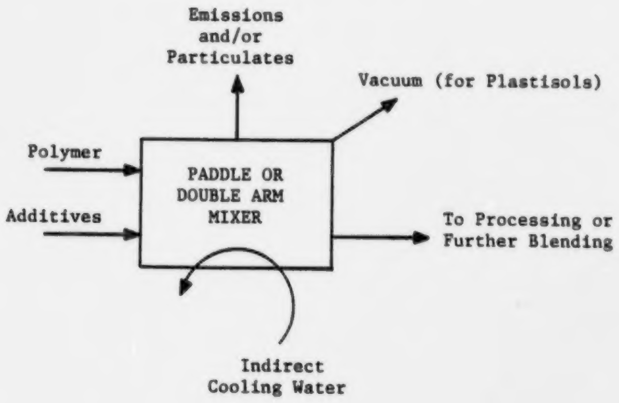
Particulate emissions could be anticipated from loading and unloading operations. Volatile emissions are possible from residual monomer, degraded plastics, and volatile additives in liquid and flux melt operations. Water used for cleaning operations is the sole wastewater source. In some operations with frequent additive and polymer changes large amounts of cleaning water can be generated.

Intensive Vortical Action Mixers - These mixers provide rapid blending of polymers, in particular PVC. The polymer is preheated, and then additives are loaded into the mixer. A high speed impeller blade at the base of the bowl mixes the polymer in five to 10 minutes. The rotating speed of the impeller produces the shear and generates heat. For dry solids impeller speeds range from 80 to 160 rpm.[72] For liquids and pastes impeller speeds can range from 500 to several thousand rpm.[26] Variations in impeller design are used for a wide variety of applications. These blenders can be utilized for dry solids preblending and for liquid and paste blending. Emissions are vented from the vortex of the blender. Heating and cooling waters do not contact the product. A block diagram of the intensive vortical action mixer is shown in Figure 18. Both particulate and volatile emissions are possible.

Banbury Mixers - Mainly designed for batch operations, these mixers blend the polymer via elliptical rotor blades which operate in a confined space. Polymer contact with the blades is maintained by a pressure ram. The amount of heat generated requires noncontact cooling water to prevent excessive polymer degradation. Figure 19 depicts a block diagram of the Banbury mixer. Vinyls, polyolefins, ABS, styrene, and thermosets (melamine and urea) can be blended in the Banbury mixer. These mixers generally feed extruders or two roll mills.

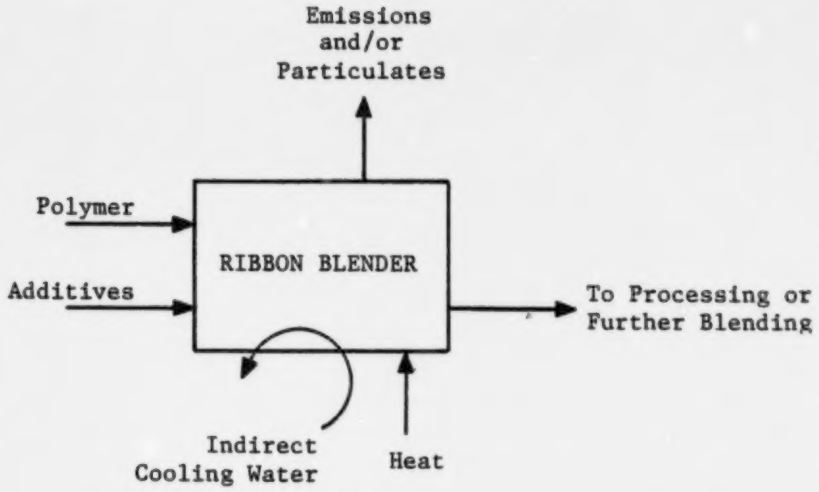

Particulates
Polymer Resin
Additives
CONICAL MIXER WITH ORBITING SCREW
To Processing or Further Blending

CONICAL MIXERS WITH ORBITING SCREW

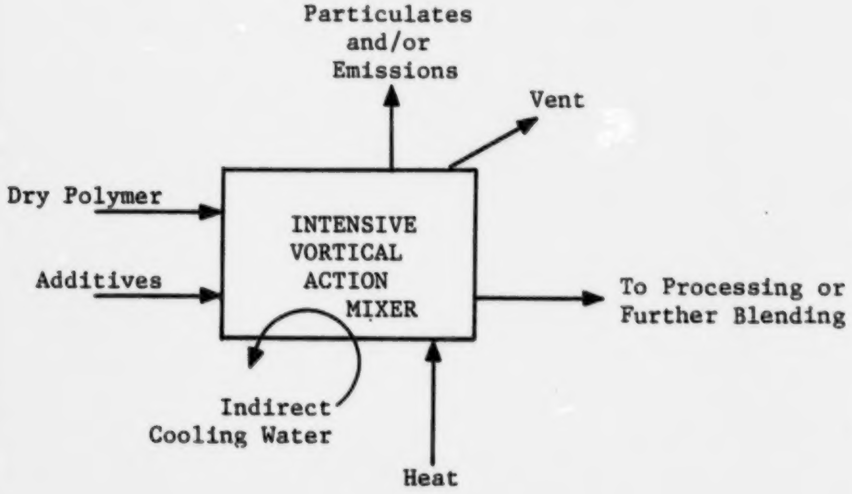

Emissions and/or Particulates
Vacuum (for Plastisols)
Polymer
Additives
PADDLE OR DOUBLE ARM MIXER
To Processing or Further Blending
Indirect Cooling Water

PADDLE AND DOUBLE ARM MIXERS

Figure 17.


Emissions and/or Particulates
Polymer
Additives
RIBBON BLENDER
To Processing or Further Blending
Indirect Cooling Water
Heat

RIBBON BLENDER


Particulates and/or Emissions
Vent
Dry Polymer
Additives
INTENSIVE VORTICAL ACTION MIXER
To Processing or Further Blending
Indirect Cooling Water
Heat

INTENSIVE VORTICAL ACTION MIXERS

Figure 18.

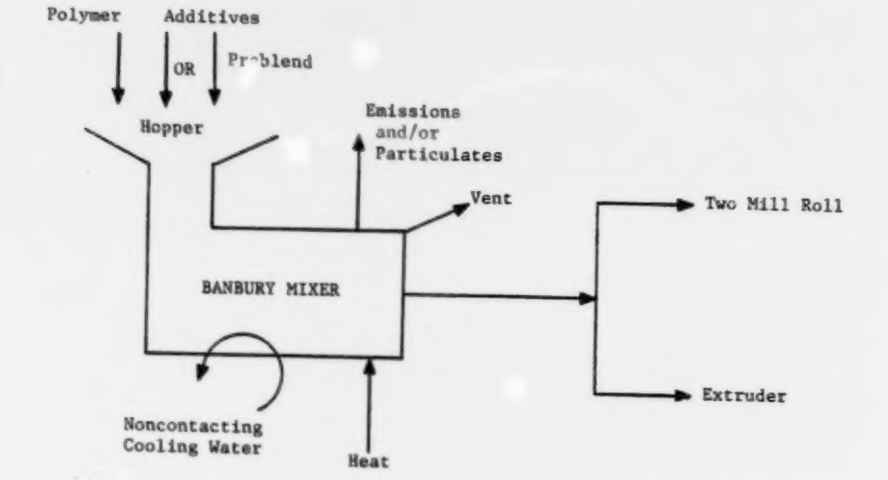

Polymer
Additives
OR
Pr-blend
Hopper
Emissions and/or Particulates
Vent
Two Mill Roll
BANBURY MIXER
Extruder
Noncontacting Cooling Water
Heat

Figure 19. Banbury mixer.

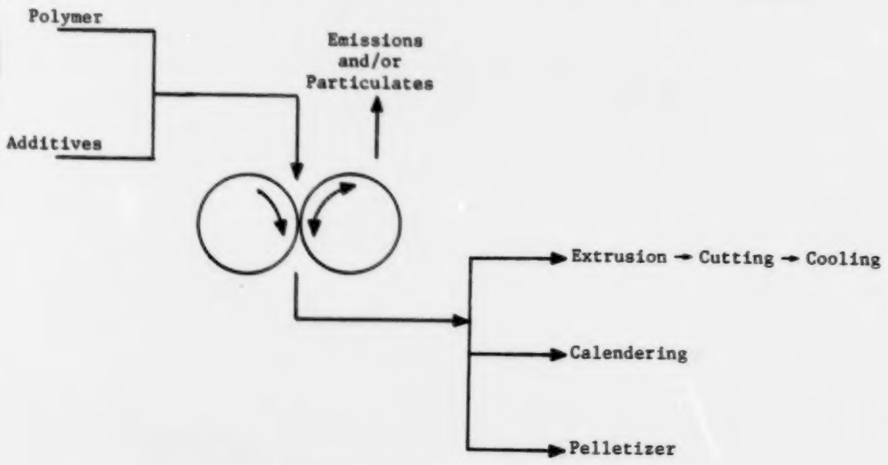

Polymer
Additives
Emissions and/or Particulates
Extrusion → Cutting → Cooling
Calendering
Pelletizer

Figure 20. Two roll mixer.

Because of the intensive mixing performed in the Banbury, frictional heat is generated, which can cause the polymer to degrade. Monomer, polymer degradation products, and volatile additives, as well as particulates, comprise the emissions. Cooling water does not contact the polymer or additives.

Two Roll Mill - The two roll mill kneads the polymer and additives between two hot rolls as shown in Figure 20. Shearing action is created by the rolls rotating at different speeds. After a specified milling time, the compounded material is stripped from the rolls.

The rolling of polymer could be expected to generate emissions. Roll temperatures average 150 to 160°C. Residual monomer and low boiling additives could be expected to volatilize. In cases where powder blends are fed onto the roll, particulate emissions could be expected. For more information on milling of polymers see Section 2 - Calendering.

Extruders - The extruder mixes and blends polymers. Polymer pellets and additives are mixed in a hopper or preblended. The resin and additives melt and mix due to the shearing action of the extruder screw. Both single and twin screw extruders are used in compounding. Polymer which has been compounded by extrusion operations can be directly processed into extruded film, sheet, or profiles or it can be pelletized for other processing operations requiring pre-formulated polymer. The extrusion process allows for flexibility in blending. For example, highly friable or abrasive additives can be added near the end of the extruder to minimize particle breakage or wear to equipment. A block diagram of extrusion is shown in Figure 21. For more information on extrusion see Section 6 - Extrusion.

Point source emissions from the extruder include particulate emissions from the hopper, cutter, shaker screen, and dryer. Volatile emissions including residual monomer, low boiling additives, and polymer degradation products could be expected from the die, the cutter, and the drier. Wastewater is generated in the water quenching and screening of the blended polymer. If cooling of an extruder is necessary, noncontact cooling water is used, and therefore wastewater is generated only during cleaning operations.

Motionless Mixers - These cylindrical mixers contain a series of stationary baffle elements which facilitate flow division and radial mixing. The geometries and pressure on the polymer determine the flow pattern and extent of mixing. These elements are especially useful in promoting uniform colorant and temperature distribution, and are commonly used with other blending equipment as mixing finishers preceding processing. Figure 22 shows a typical configuration for motionless mixers.

Emissions from motionless mixers include volatiles such as residual monomer, decomposition products, and additives. Water is not used in this process except for infrequent cleaning operations.

OPERATING PARAMETERS AND UTILITY REQUIREMENTS.

The conditions under which compounding operations are performed are strongly governed by the polymer, the additives, and the type of blending

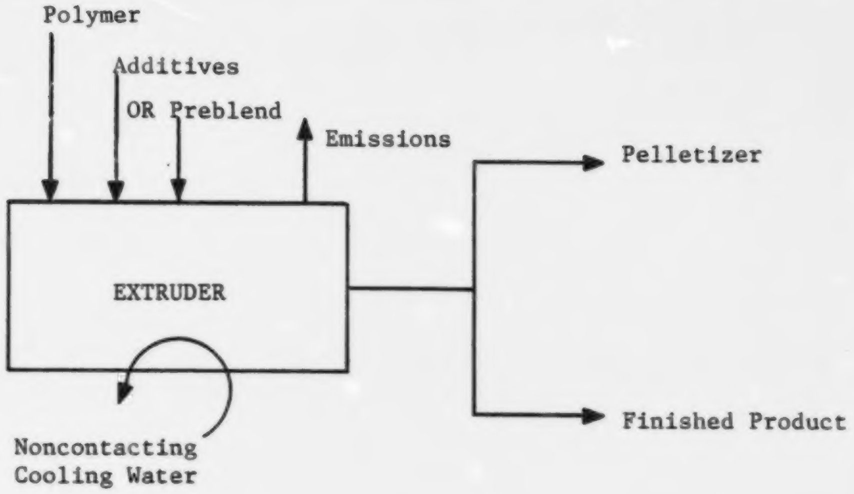

Polymer
Additives
OR Preblend
Emissions
EXTRUDER
Noncontacting
Cooling Water
Pelletizer
Finished Product

Figure 21. Extrusion.

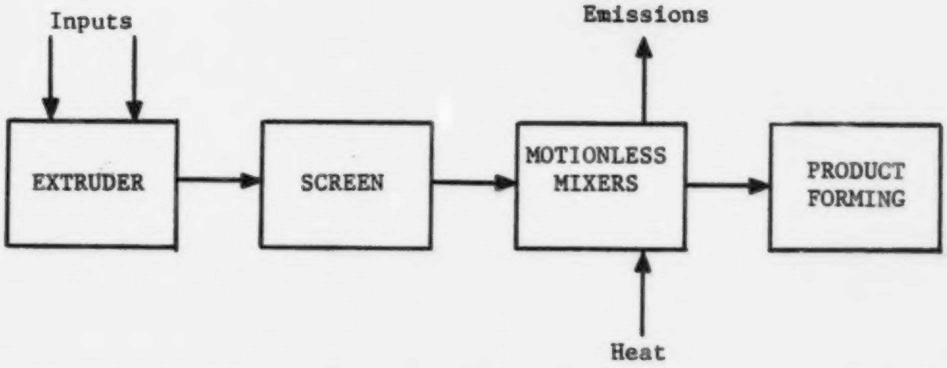

Inputs
EXTRUDER
SCREEN
Emissions
MOTIONLESS
MIXERS
Heat
PRODUCT
FORMING

Figure 22. Motionless mixers.

operations used. Most blending utilizes equipment manufacturer's guidelines to determine rough settings for temperature, pressure, and blending time. The process is then fine-tuned by trial and error to determine the optimum operating parameters.

Some typical temperatures for blending operations which are capable of maintaining heat control are given in Table 26. The wide range of temperatures illustrates the variability of blending processes. Pressure ranges typical of blending equipment are shown below.[59, 81]

Mixer	Pressure (10^6 Pascals)
Extruders	0.689 - 4.14
Motionless Mixers	137 (maximum)

Power requirements for blending operations are illustrated in Table 27. In general, high shear rates and high melt viscosities necessitate high power inputs per unit volume of polymer to achieve a uniform dispersion of additives in the melt.

WASTE STREAMS AND EMISSIONS

Compounding operations produce air emissions, wastewater, and solid waste. Table 28 presents a summary of the point source emissions from compounding operations. Emissions and wastes are discussed in more detail in the text below.

Air Emissions - All compounding operations have the potential to produce volatile and/or particulate emissions. Particulate emissions originate from loading, grinding, blending, and emptying of the blended product. Volatile emissions arise from venting of heated equipment, and consist of residual monomer, polymer decomposition products, volatile additives, and their decomposition products.

In most blending operations which utilize heat to promote mixing of the polymer, vents are included in the equipment design in order to remove volatiles including residual monomer, additives and decomposition products of the polymer and additives. Intensive Vortical Action Mixers remove volatiles from the vortex of the mixer. Extruders vent volatiles along the barrel of the screw. Paddle and Double Arm Mixers vent volatiles and may include vacuums to preserve air-sensitive mixtures.

Wastewater - Direct contact cooling water is used only as a quench for polymers blended in extruders and two mill rolls. These operations could result in dissolved additives, suspended polymer, and additive particles present in the wastewater. For a more extensive study of these waste streams, see Extrusion and Calendering.

Solid Waste - Compounding operations generate only minimal amounts of solid waste. Off-spec product could be anticipated to make the major contribution.

TABLE 26. TYPICAL OPERATING TEMPERATURES FOR MIXERS

Mixer	Polymer	Typical Temperature (°C)
Paddle and Double Arm Mixers	PVC	32
	Polyphenylene Sulfide	260 (dry)
Ribbon Blenders	PVC	80 - 100
Intensive Vortical Action Mixers	PVC	80 - 120
	Polyolefins	50 - 60
Banbury Mixers	PVC	130 - 170
	Amino Resins	50 - 80
	ABS	150 - 250
	Polyphenylene Sulfide	325 - 360
Two Roll Mills	PVC	150 - 160
	ABS	160
	Phenolics	95 - 115
Extruders	Low Density PE	250 - 260
	Linear Low Density PE	250 - 260
	High Density PE	250
	Polystyrene	125 - 230
	Polypropylene	200 - 280
	ABS	150 - 250
	SAN	175 - 230
	Polyphenylene Sulfide	302 - 357
	Polycarbonates	220 - 350
	Phenolics	280 - 340
	Polyvinylidene Chloride	198 - 210
	Polyamides	205 - 415
Motionless Mixers	Polyethylene	205
	Polystyrene	225
	Polypropylene	230
	ABS	220

Sources: Agranoff, Joan (ed). Modern Plastics Encyclopedia 1981-1982, p. 91.
Bikales, Norbert M. (ed). Encyclopedia of Polymer Science and Technology, (Vol:pp): 4:123; 10:749; 11:611; 14:420-422, 429, 572.
Gaylord, Norman G. (ed). Encyclopedia of Polymer Science and Technology, (Vol:pp): 1:431; 2:35.
Grayson, Martin (ed). Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Edition, (Vol:pp): 1:450; 16:396, 429, 466; 18:804.
Schott, N. R., B. Weinstein, and D. LaBombard, "Motionless Mixers," Chemical Engineering Progress, 1975,pp. 56-57.
Shreve, R. N., and J. A. Brink, Jr., Chemical Process Industries, 4th edition, 1977, p. 83.

TABLE 27. TYPICAL MIXERS SIZES, OUTPUTS AND DRIVE POWERS

Extrusion	Output Capacity (kg/hr)	Power Drive (Maximum) (KW)
Single Screw Extruder	200 - 500	90
	600 - 1,400	190
	1,600 - 3,500	550
Twin Screw Extruder	450	74
	1,600	257
	5,000	882
High Intensity Banbury Mixer	1.0 - 15.6 KW/kg	

Source: Funt, John M., Mixing of Rubbers, 1977, pp. 5/43, 6/22, 6/23.

TABLE 28. COMPOUNDING POINT SOURCE EMISSIONS

	Air Emissions						Wastewater				Solid Waste			
	Particulates			Volatiles										
	Polymer	Colorants	Other Additives	Monomer	Plasticizer	Other Additives	Polymer	Plasticizer	Colorants	Other Additives	Polymer	Plasticizer	Colorants	Other Additives
Granulators	X													
Ball Mills	X	X	X	X	X	X								
Tumble Blenders	X	X	X											
Gravity Mixers	X	X	X											
Conical Mixers w/Orbiting Screws	X	X	X											
Paddle and Double Arm Mixers	X	X	X	X	X	X								
Ribbon Blenders	X	X	X	X	X	X								
Intensive Vortical Action Mixers	X	X	X	X	X	X								
Banbury Mixer	X	X	X	X	X	X								
Two Mill Rolls	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Extruders	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Motionless Mixers				X	X	X								

WORKER DISTRIBUTION AND EXPOSURE

Although the combinations of polymers and additives which may be compounded are virtually unlimited, the operations employed in polymer compounding are relatively simple. Estimates of worker distribution determined by correlating major equipment manhour requirements with the process diagrams shown in Figures 16 through 22, are given below:

Unit	Workers/Unit/8-hour Shift
Loading/Drying/Preblending	1.0
Compounding	1.0
Drying	0.5
Flaking	0.25
Screening	0.25
Bagging/Packaging	1.0

The diversity of materials blended in compounding operations makes estimating worker exposure parameters difficult. However, for reference purposes, Table 29 summarizes the major workplace contaminants which could result from compounding operations. The equipment from which they could be released is listed in Table 30. Toxicity information for these chemical substances and physical agents is summarized in Appendix C of this document and discussed in detail in IPPEU Chapter 10b.

TABLE 29. MAJOR CONTAMINANTS GENERATED FROM PLASTICS COMPOUNDING OPERATIONS

Polymer Particulates

Antiblocking Agents (for polyvinyl chloride) - silicates
- waxes

Antioxidants (for polyolefins, polystyrene, ABS) - amines
- alkylated phenols
- phosphates
- thio compounds

Blowing Agents - azodicarbonamide
- azobisisobutyronitrile
- methylene chloride

Blow Agent By-Products - N_2
- CO
- CO_2
- tetramethylsuccinonitrile

Colorants - carbon black
- titanium dioxide
- Cd sulfoselenide
- phthalocyanines
- anthroquinone red
- monoazo yellow

Crosslinking Agents (for polystyrene) - divinyl benzene
(for polyethylene) - organic peroxides

Curing Agents (for polyesters, amino resins, phenolics) - azo compounds
- peroxides
- amines

(for polyurethanes) - organo tin compounds
- amines

Fillers - Ca carbonate
- kaolin
- diatomaceous earth
- marble dust
- iron filings
- plaster
- vermiculite
- wood dust
- talc (no asbestos)

(continued)

TABLE 29 (continued)

Flame Retardants - antimony oxide
- alumina trihydrate
- trixylenyl phosphate
- decabromodiphenyl oxide
- chlorinated paraffin wax

Heat Stabilizers (for polyvinyl chloride and polyvinylidene chloride) - tribasic Pb sulfate
- Ba/Cd stearate
- Ca/Zn stearate

Lubricants - hydrocarbon oils
- paraffin waxes
- amides

Mold Release Agents - silicone
- chlorofluorocarbons
- waxes
- mica
- talc

Plasticizers - di-n-octyl phthalate
- diisooctyl phthalate
- diisodecyl phthalate
- tricresyl phosphate
- di-(2-ethylhexyl) phthalate

Reinforcing Agents - asbestos
- silica
- glass fibers

Slip Promoters (for polyvinyl chloride) - silicates
- waxes

UV Stabilizers - benzotriazides
- benzophenones

TABLE 30. POTENTIAL CONTAMINANTS FROM COMPOUNDING EQUIPMENT

Equipment	Chemical Substance or Physical Agent
Tumble Blender	Polymer particulates (particularly amino resins) Colorant particulates Miscellaneous additive particulates Noise
Gravity Mixer	Polymer particulates Additive particulates Noise
Conical Mixer	Polymer particulates Additive particulates Noise
Paddle/Double Arm Mixer	Volatile monomer (particularly formaldehyde) Volatile plasticizer Miscellaneous volatile additives Noise
Ribbon Blender	Polymer particulates (primarily polyvinyl chloride) Additive particulates Volatile monomer (possibly vinyl chloride) Volatile plasticizer Miscellaneous volatile additives
Intensive Vortical Action Mixer	See Ribbon Blender
Banbury Mixer	Polymer particulates (particularly vinyls, polyolefins, ABS, polystyrene, amino resins) Additive particulates Volatile monomer, including - vinyl chloride - 1,3-butadiene - styrene - acrylonitrile - ethylene - propylene - vinylidene chloride Noise
Motionless Mixer	Volatile monomer Volatile plasticizer Miscellaneous volatile additives
Granulator	Polymer particulates

SECTION 6

EXTRUSION

FUNCTION

Extrusion processing refers to the forcing of molten polymer under pressure through a shaping die, resulting in products of uniform cross-sectional area such as pipe, tubing, sheet, film, and profile. The process has a number of different applications, including the production of pellets and parisons (blow molding preforms) for later use, and the production of finished and semi-finished products. Extrusion accounts for the processing of more pounds of plastics than any other process.[136] At some point in the conversion of raw resin to consumer product, 60 percent of all thermoplastics undergo some form of extrusion.[121] Extrusion produces a wide variety of products including:

- pellets for further processing;
- pipe, tube, and other profile shapes;
- parisons for blow molding;
- monofilaments;
- film;
- sheet;
- wire and cable coating; and
- coextruded (multi-layer) products.

There are two basic types of extrusion processing: ram extrusion and screw extrusion. The earliest method of extrusion was performed with ram extrusion. In this operation, a moving piston rams molten polymer through a die. Pressures in this slow process can go as high as 3.45×10^7Pa (50,000 psi).[15] Screw extrusion relies on the rotation of a screw within a cylinder to meter, mix, and force the molten polymer through a die. Pressures required for this process are less than those resulting from ram extrusion.

The ram extrusion method is used to produce certain profile sections from thermoset plastics, including silicones, phenolics, melamines, epoxies, and alkyds. This method of thermoset processing is not in widespread commercial use since it cannot compete economically with the compression or transfer molding of thermosets. Thermoplastics, such as polytetrafluoroethylene (PTFE), usually cannot be processed using screw extrusion as other conventional thermoplastics due to their exceptionally high melt viscosities and are often ram extruded. Granular PTFE is ram extruded at very slow rates whereas PTFE powder is made into a paste with naphtha and is ram extruded at or slightly above room temperature. After extrusion, the product is heated, thereby volatilizing the naphtha and potentially producing a source of air pollution.[10]

Ram extrusion does not provide the versatility and quality uniformity that today's continuous screw extrusion operations provide. Since a very small percentage of the final extrusion products are produced using ram extrusion, it will not be discussed further. The remainder of this section will discuss the various applications of screw extrusion.

Extrusion systems are often used for formulation operations. Additives such as specialty chemicals, plasticizers, UV stabilizers, and colorants can be blended in the screw extruder cylinder. The formulated polymers are then either extruded to the product shape, or are formed into parisons or pellets for subsequent processing. The use of extrusion systems for formulation operations is further described in the Compounding section of this document.

INPUT MATERIALS AND PRODUCTS

A wide range of polymers are used in screw extrusion operations. It is estimated that 20 percent of all plastic consumer products are extruded into their final shape.[207] Polymers which can be used as input materials to screw extrusion processing are:

- Acrylic Resins
- Acrylonitrile-Butadiene-Styrene (ABS)
- Aromatic Polyester
- Fluoroplastics
- Nylon
- Polyacetal
- Phenylene Oxide
- Polybutylene
- Polycarbonate
- Polyethylene
  - Low Density (LDPE)
  - Linear Low Density (LLDPE)
  - High Density (HDPE)
  - High Molecular Weight (HMWPE)
  - Ethylene-Vinyl-Acetate (EVA)
- Polypropylene
- Polystyrene
- Polyurethane
- Polyvinyl Chloride (PVC)
- Styrene-Acrylonitrile (SAN)
- Sulfone Polymers
- Thermoplastic Polyesters (PBT & PET)
- Vinylidene Chloride

Each polymer must be formulated in order to provide the properties necessary in the final product. Polymers can be formulated at one or both of two different steps in their processing sequence. Immediately after their production, polymers may be formulated and pelletized to provide processors with polymer grades specific for a subsequent processing step. Polymers can also be formulated within the extruder screw during extrusion of the semi-finished or final product. Colorants and pigments are most often blended at this time. These blending processes, and the additives which go into them are discussed in more detail in the Compounding section of this document. Additive "recipes" are designed specifically for a polymer application and are usually considered proprietary information by processors. Table 31 delineates polymers, generalized formulations, and products of the extrusion process. More detailed information on the major plastics additives used in extrusion can be found in the Industry Description section of this document.

TABLE 31. INPUT MATERIALS AND PRODUCTS IN EXTRUSION

Polymer	Formulation	Extrusion Process	Products
Acrylonitrile-Butadiene-Styrene (ABS)	Polymer dried 2 to 4 hrs at 82-93°C (180-200°F) in dehumidifying circulating air hopper. Antioxidants Blowing Agents Colorants Flame Retardants Lubricants UV Stabilizers	Profile, Pipe, and Tubing	Pipe for natural gas, water, and chemicals Tubing Complex profiles Drain, waste, and vent pipes Door jambs and slides Handles
		Sheet	Sheet for thermoforming into furniture, luggage, building and construction products, interior auto panels, boats and canoes, camper tops, refrigerator doors and inner liners, refrigerator crisper trays, toys, shower stalls, and bathroom fixtures.
		Coextrusion	Multilayer profile and sheet
Acetal Homopolymer and Copolymer	Antioxidants Blowing Agents Colorants Fillers Lubricants Reinforcers Stabilizers UV Stabilizers	Profile, Pipe, and Tubing	Tubing for plumbing Rods Slabs
		Sheet	Sheet to be machined into industrial parts and appliance housing
		Wire and Cable Coating	Wire
Acrylic Resins	Predried to less than 0.25% moisture	Profile, Pipe, and Tubing	Profiles for appliances and automobiles
	Blowing Agents Colorants Flame Retardants Impact Modifiers UV Stabilizers	Sheet	Sheet for lighting fixtures, signs, housewares, and personal accessories

(continued)

TABLE 31 (continued)

Polymer	Formulation	Extrusion Process	Products
Fluoroplastics			
Polytetrafluoroethylene (PTFE)	Fillers	Profile, Pipe, and Tubing	Rods, sheets, and tubes Spaghetti Tubing
		Film	Tape
		Wire and Cable Coating	Wire and cable insulation for hookup wire, coaxial cable, interconnecting wire, computer wire, and electrical T's.
Fluorinated Ethylene Propylene Copolymer (FEP) Teflon®		Profile, Pipe, and Tubing	Tubes for Linings Rod Monafilament
		Sheet	Sheet
		Film	Film for use as glazing in solar energy collectors
		Wire and Cable Coating	Wire and cable
Ethylene-Tetrafluoro-Ethylene Copolymer (ETFE) (Tefzel®)		Profile, Pipe, and Tubing	Tubing Monofilaments
		Film	Film
		Wire and Cable Coating	Wire and cable Insulation
Polychlorotrifluoro Ethylene (PCTFE)		Profile, Pipe, and Tubing	Rod and tubing Medical tubing
		Film	Film for packaging, blister packs, tapes, and drugs. Aerospace components
Ethylene-Chlorofluoro Ethylene Copolymer (ECTFE)		Profile, Pipe, and Tubing	Pipe linings Laboratory tubing
		Film	Film
		Wire and Cable Coating	Wire and cable for mass transit and power plants

(continued)

TABLE 31 (continued)

Polymer	Formulation	Extrusion Process	Products
Fluoroplastics (Continued)			
Polyvinylidene Fluoride (PVDF)	Colorants Fillers Plasticizers	Profile, Pipe, and Tubing	Monafilament Heat Shrink Tubing Rigid Pipe
		Sheet	Sheet
		Film	Film
		Wire and Cable Coating	Wire and Cable Insulation
Polyvinylfluoride (PVF)		Film	Film for use as laminates on wood, plastic, and metals for aircraft interiors, automobile exterior, trim rails, aluminum and hardboard building panels and siding, roofing membranes, and institutional wall covering.
Nylon 6/6 and Nylon 6	Polymer dried 4 to 10 hrs at 110°C (230°F) or vacuum drying at 70 to 80°C. Antiblocking Agents Antioxidants Antistatics (not generally used) Colorants Flame Retardants Fillers Heat Stabilizers Lubricants Nucleating Agents Plasticizers Reinforcers UV Stabilizers	Profile, Pipe, and Tubing	Rods Guides and channels Tubing for automotive air conditioners, radiator over-flows, compressed air tools, and food processing. Monofilaments for toothbrushes, hairbrushes, paint brushes, fishing line, coil zippers, and waistband stiffeners. Tape for strapping.
		Film	Packaging film for processed meats and cheeses
		Wire and Cable Coating	Automotive cables Industrial cables Aircraft cables
Modified Phenylene Oxide	Colorants Flame Retardants Polymeric Modifiers	Wire and Cable Coating	Cable

(continued)

TABLE 31 (continued)

Polymer	Formulation	Extrusion Process	Products
Polybutylene		Profile, Pipe, and Tubing	Pipe
		Film	Film
Polycarbonate	Antioxidants Blowing Agents Colorants Reinforcers UV Stabilizers	Profile, Pipe, and Tubing	Tubing and Rod Stock
		Sheet	Sheet for signs Refrigerator Shelves
		Film	Film
Thermoplastic Polyester Polybutylene Terephthalate (PBT) and Polyethylene Terephthalate (PET)	Polymer dried 2 to 4 hrs at 150-180°C (302-356°F). Antioxidants Colorants Fillers Flame Retardants Reinforcers	Sheet	Sheet for packaging, conveyor belts, snap-roll sheeting, spacers, and drum heads. Photographic film for X-rays, industrial, professional still photography, graphic arts, and microfilm. Magnetic tape for audio, video, computers, and instrumentation. Insulating Tape Packaging film for meat wrap, boil-in-bag pouches, cheese wrap, snack foods, battery labels, and cigarette wrap Matte Finish Drafting Film Book Covers Carbon Films Reinforcement edging for paper, sheets and tabs Typewriter Ribbons Tape Backing Metallized Film Pipe Wrap

(continued)

TABLE 31 (continued)

Polymer	Formulation	Extrusion Process	Products
Aromatic Polyester		Profile, Pipe, and Tubing	Rod Tubing Profiles
Low Density Polyethylene (LDPE)	Antiblocking Agents Antioxidants Antistatics Colorants Fillers Flame Retardants Impact Modifiers Reinforcers UV Stabilizers	Profile, Pipe, and Tubing	Pipes for cold water, conduits, profiles, tubing, handles, straps, bumpers and edgings and guides
		Film	Food packaging film for baked goods, produce, candy, frozen food, meat and poultry, soft drink cases, butter and lard, noodles and dry foods, dried vegetables, snack foods, and cereal. Industrial liners and shipping sacks Pallet shrink film and wrap Bags and packaging for garment bags, ice cube packaging, hardware packaging, yarn cone wrap, paper goods packaging, boxed chemicals wrap, trash bags, sandwich bags, disposable diapers, and separator sheets
		Sheet	6-pack can carriers
		Coextrusion	Multilayer profile and sheet
	Antioxidants Carbon Black Crosslinking Agents UV Stabilizers	Wire and Cable Coating	Wire and cable coatings for power cable

(continued)

TABLE 31 (continued)

Polymer	Formulation	Extrusion Process	Products
High Density Polyethylene (HDPE)	Antioxidants Antiblocking Agents Antistatic Agents Blowing Agents Colorants Crosslinking Agents Flame Retardants Impact Modifiers Reinforcers Stabilizers UV Stabilizers	Profile, Pipe, and Tubing	Pipe fittings and liners Conduits Profiles Large sewer pipes Straps and belts Rods Corrugated tubing for drainage in agriculture and commercial and industrial construction
		Film	Film for packaging Glassine-like paper for potato chip packaging, florist's paper, and merchandising bags
		Sheet	Sheet for 6-packs cans Seats Recreation objects Dunnage bins Tote bins
		Wire and Cable Coating	Wire and Cable
High Molecular Weight Polyethylene (HMWPE)	Antioxidants Antistatics Colorants Fillers	Profile, Pipe, and Tubing	Industrial pipe
		Film	Film for merchandise bags, shipping sacks and thermoforming
Ethylene Vinyl Acetate (EVA)	Reinforcers	Profile, Pipe, and Tubing	Hose Weather stripping Medical tubing
		Film	Film for packaging and laminates
		Wire and Cable Coating	Wire and cable
		Coextrusion	Multilayer profile and sheet
Polyethylene Oxide		Profile, Pipe and Tubing	Water pipes Water treatment applications

(continued)

TABLE 31 (continued)

Polymer	Formulation	Extrusion Process	Products
Polypropylene	Antiblocking Agents Antioxidants Antistatic Agents Blowing Agents Colorants Fillers Flame Retardants Plasticizers Reinforcers Stabilizers UV Stabilizers	Profile, Pipe, and Tubing	Profile Pipes and conduits Soda straws Weather stripping Hinges and baffles Carpet backing Ropes and cordage Bags and bagging Bristles Upholstery fabrics Pen bodies
		Film (heat set and shrink wrap)	Film for packaging of snack foods, candy, pet food, cigarette packages, textiles, men's shirts, women's hosiery, baked goods and fresh produce, cheese, cookie wraps, phonograph records, toys, games, housewares, irregular shaped items, and processed food pouches
		Sheet	Sheet for thermoforming blister packs Packaging boards Crating
		Wire and Cable Coating	Wire and cable insulation for telephone wires and waterproof cables
		Coextrusion	Multilayer profile and sheet
Polystyrene	Antioxidants Antistatics Blowing Agents Colorants Corrosion Inhibitors Flow Improvers Flame Retardants Inhibitors Light Stabilizers Mixing Aids Mold Release Agents Reinforcers Stabilizers UV Stabilizers	Profile, Pipe and Tubing	Filaments for decorating and brush bristles Trim strips Door guides Profiles Shower doors Partitions
		Sheet	Sheet for thermoforming dairy containers, cups, lids, and single service packs Refrigerator components
		Film	Film for packaging

(continued)

TABLE 31 (continued)

Polymer	Formulation	Extrusion Process	Products
Polyurethane	Blowing Agents Colorants Flame Retardants	Sheet	Sheet for leather "like" finishes
		Wire and Cable Coating	Wire
Polyvinyl Chloride (PVC)	Antiblocking Agents Antioxidants Blowing Agents Colorants Diluents Fillers Flame Retardants Heat Stabilizers Impact Modifiers Lubricants Plasticizers Reinforcers UV Stabilizers	Profile, Pipe, and Tubing	Monofilaments Pipes and conduits Weather stripping Gutters Window profiles Garden hoses Medical tubing Irrigation pipe Pipe fittings Flooring Water supply pipes Agricultural and irrigation pipes Vent pipes Rain gutters Molding
		Film	Film for packaging of meat and produce
		Sheet	Sheet for thermoforming for baby pants, inflatable toys, footwear, outerwear, credit cards, pool liners, table covers, shower curtains, bedspreads, and draperies, and garment bags Flooring Wall covering Siding Shutters
		Wire and Cable Coating	Wire and cable for buildings, automobiles, communications and signals Flexible cord for lamps, extension cords and appliances
		Coextrusion	Multilayer profile and sheet

(continued)

TABLE 31 (continued)

Polymer	Formulation	Extrusion Process	Products
Styrene-Acrylonitrile (SAN)	Polymer dried 2 hrs at 71-82°C (160-180°F) UV Stabilizers Elastomers	Sheet	Sheet for thermoforming into appliance and automobile parts such as instrument panel windows
Sulfone Polymers		Profile, Pipe, and Tubing	Medical tubing
Vinylidene Chloride	Antioxidants Heat Stabilizers UV Stabilizers	Profile, Pipe, and Tubing	Filaments Rods Tubing and Pipe
		Film	Film

Sources: Agranoff, J. (ed). Modern Plastics Encyclopedia, 1981-1982, pp. 4, 8, 32, 49, 50, 58, 60, 64, 70, 89, 90, 100, 110, and 334.

Beadle, J. D., Plastics Forming, 1971, p. 77.

Bikales, Norbert M. (ed). Encyclopedia of Polymer Science and Technology, (Vol:pp), 10:105-109, 13:397-398, 14:570-753,

Chemical Economics Handbook, 1976 Plastics, Volumes 1 and 2.

Fisher, F. G., Extrusion of Plastics, 1976, p. 178.

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Griff, A. L., Plastics Extrusion Technology, 1968, p. 69.

Milby, R. V., Plastics Technology, 1973, p. 406.

Mock, John A., "Additives 1982 - A Multiplicity of Problem Solvers," Plastics Engineering, June 1982, p. 29-38.

Rauch, James A., The Kline Guide to the Plastics Industry, 1978, pp. 48, 54, 60, 64, 68, 70, 74, and 77.

Standen, A. (ed). Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, (Vol:pp), 19:109-112, 21:270-274.

There are hundreds of typical extrusion formulations. PVC pipe is a well-known example of an extrusion product, and a typical formulation for extrusion-grade PVC pipe is given below:[137]

Material	Parts by Weight
PVC (resin)	100
Tin Stabilizer	0.4
Parraffinic Lubricant	1-1.3
Oxidized Polyethylene	0.2-0.25
Calcium Stearate (lubricant)	0.4-0.8
Titanium Dioxide (colorant)	1-1.5
Acrylic Processing Aids	0-1.5
Calcium Carbonate (filler)	2

PROCESS DESCRIPTION

Although screw extrusion produces a wide variety of final products, the general description of the screw extrusion process is similar. Thermoplastic polymer granules, pellets, powder, or beads, are fed into the hopper of the extruder. Particulate emissions may be generated during this feeding operation. The polymer is picked up by a rotating screw within the extruder cylinder and is forced toward the die. Heat provided to the cylinder walls by electricity, steam, or oil heat, begins the softening of the polymer pellets. As the material moves along the cylinder, the friction generates additional heat which becomes the primary heating mechanism. Indirect cooling water or air is used to remove excess heat in order to maintain the proper processing temperature. During this heating and compression period, the plastic is transformed into a homogeneous melt and is thoroughly mixed. Emissions liberated during these operations are usually vented from the extruder barrel. This provides for uniform consistency when color blending is performed or special additives are incorporated.

The extruder screw is the critical component of the extruder assembly. Screw design is optimized for the particular polymer being extruded and the desired product. A screw consists of three sections: feed, transition, and metering. The feed section conveys the solid pellets forward from the hopper and into the transition section where the depth of the screw flight decreases. Here the polymer is compacted and pressed against the hot barrel, where both frictional and conducted heat produce the melt. The metering section thoroughly mixes the melt and pushes the molten polymer out through the extrusion die at a controlled (i.e., metered) rate.

Extruders can be designed as single-screw or twin-screw extruders. Single-screw extruders are mechanically the simpler of the two and are capable of providing quality products for certain polymer applications. Figure 23 presents a schematic of a single-screw extruder assembly. Twin-screw extruders provide much better mixing of the polymer between two intermeshing screws. Figure 24 presents a schematic of a twin screw extruder assembly. Twin-screw extruders are used extensively in polymer compounding and formulating operations, color blending, and for extruding difficult materials such

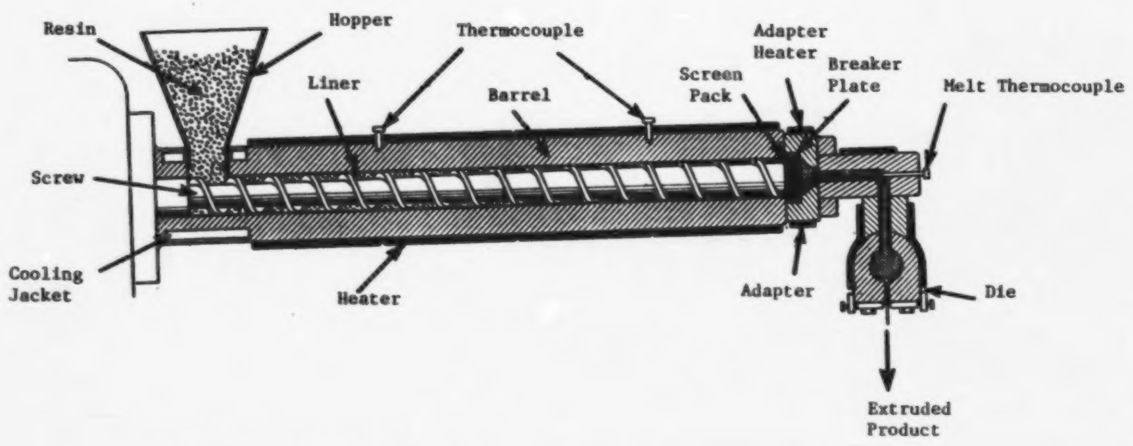
Resin
Hopper
Thermocouple
Adapter Heater
Breaker Plate
Screen Pack
Melt Thermocouple
Liner
Barrel
Screw
Cooling Jacket
Heater
Adapter
Die
Extruded Product

Figure 23. Schematic of a single-screw extruder.

Source: Rodriquez, F. Principles of Polymer Science. McGraw-Hill, Inc., New York, New York, 1970. p. 323.

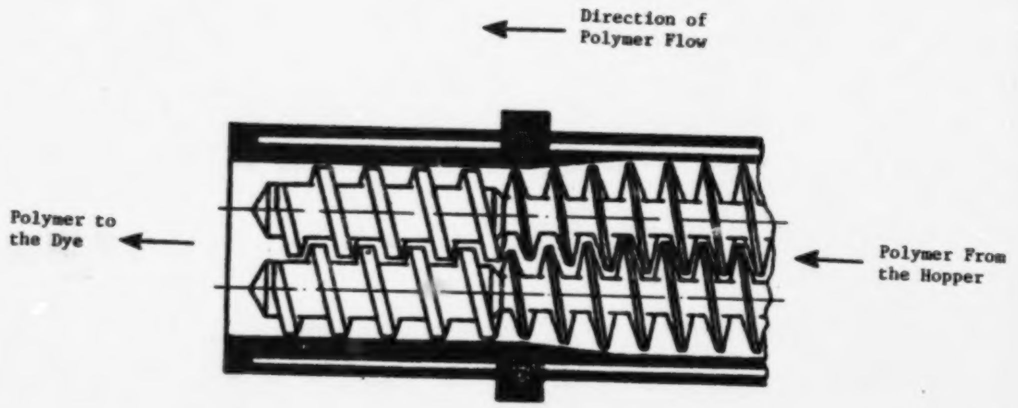
Direction of
Polymer Flow
Polymer to
the Dye
Polymer From
the Hopper

Figure 24. Schematic of a twin-screw extruder.

Source: Schwartz, Seymour S. and Sidney H. Goodman. Plastics Material and Processes. Van Nostrand Reinhold Company, Inc., New York, New York, 1982.

as PVC powder blends for pipe, siding, and other products.[59] In the extrusion of such materials in a twin-screw extruder, the frictional heat build-up is much lower than in a single-screw extruder. The output of a twin-screw extruder is about three times that of a single-screw extruder of the same screw diameter and speed; however, in normal operation, twin-screw speeds are less than those of single-screw machines.[59]

Typical formulations for extruding rigid or soft PVC on a twin-screw extruder are shown below:[126]

Material	Parts by Weight	
	Rigid Pipe	Soft Pipe
PVC Resin	100	100
Plasticizer (commonly dioctyl phthalate)	---	60
Stabilizer	2.5-3	2
Lubricant	3-3.5	2.5

Extruders are normally specified by screw diameter and length to diameter ratios. Diameters range from one inch in small production extruders to 20 inches for large scale operations.[177] Laboratory extruder screws are found with diameters as small as 3/4-inch. Typical L/D (length to diameter) ratios are in the 20:1 to 36:1 range.[177] Diameters, length to diameter ratios, and screw design are specified to provide the best melt, mix, and feed properties of the polymer being processed.

Just prior to leaving the extruder cylinder, the melted polymer passes through a screen pack which removes dirt and provides back pressure control. The melt enters the die at high pressure. The extrusion die is a streamlined orifice that reduces the melt to the desired shape (e.g., sheets, tubing). The die orifice size is designed to be slightly larger than the desired product size to allow for draw and shrinkage during the subsequent cooling operations. As the extrudate leaves the extruder, it is transported over some type of roller or conveyor cooling system which cools the hot extrudate by use of air or water. A cooling water waste stream may be produced by the cooling operations. The rate at which the extrudate is transported, or the "takeoff rate", influences the dimensions of the final product. After cooling, it is continuously fed to other processing steps such as cutting, sealing, coating, or packaging.

Variations from this general screw extrusion description and specific information on the six general areas of extrusion according to product are given below.

Pelletizing - Extrusion processes are often used to blend, color, and granulate thermoplastic polymers after they are produced and before they are shipped to the processor. Commonly pelletized thermoplastics are ABS, polyethylene, polypropylene, polystyrene, and PVC. Additives required for special applications and colors desired by the processor are added to the resin and are fed to the extruder to become a homogeneous melt. The melt is extruded through a multi-opening die. The melt is taken off as strands which, after cooling, are cut into pellets of the desired size. In many cases, the pellets are cut at the face of the die, which is submerged in water for rapid cooling. Screening and drying are then required before the pellets are packaged. Another common dicing procedure utilizes the "stairstep" dicer which passes a sheet of about 0.318 cm (0.125 in) thickness through a device which cuts it into cubes.[177] Pellets are usually pneumatically conveyed into storage hoppers from which they are packaged for shipment to processors. Particulate emissions can be generated during such cutting and packaging operations. Pelletized polymers can be in the form of round, cylindrical, or cube-shaped particles and can be used as feed to product extrusion, molding, casting, foaming, and other processing operations. A block diagram of pelletizing extrusion is shown in Figure 25.

Profile, Tube, and Pipe - Extrusion operations are used to produce profiles, tubes, and pipes from a wide variety of thermoplastics; the most commonly used polymers are ABS, LDPE, HDPE, polypropylene, polystyrene, and PVC.

The most critical aspect of profile, tube, and pipe extrusion is the proper design of the die. The properties of the polymer to be extruded, as well as the functions of the profile, must be taken into consideration when the die is designed. Hollow tubes, pipes, and profiles require air to be blown into the hollow areas until the extruded polymer has sufficiently hardened to hold its shape. Profiles and tubing are cooled after leaving the extruder either by submersion in a water bath, or by air. Water bath submersion produces a cooling water waste stream. Vacuum sizing may be used to maintain closer control on the product specifications. Cooled pipe, tube, and profile are transported over rollers to cutting or wind-up operations. Cutting operations may produce particulate emissions. A block diagram of profile, tube, and pipe extrusion is shown in Figure 26. Typical products include conduits, edgings, sewer pipes, pipe liners, soda straws, weather stripping, garden hose, medical tubing, and irrigation pipe.

Monofilaments are produced in a similar manner except that the hot filament leaving the extruder die is stretched by moving the guide rollers faster than the filament is being extruded. This stretching monoaxially orients the fibers, which raises their tenacity or tensile strength. The orientation is typically done after the extruded filament has solidified by reheating the fibers and then stretching them. Monofilaments are cut to the desired length or wound onto beams or tubes as continuous filament. Nylon, polypropylene, polyethylene, polystyrene, and PVC are commonly processed into monofilaments.

Parisons for blow molding operations (see Section 13) are formed by rod or tube extrusion. Extruders are often used to directly feed blow molders with molten parisons. In situations where the parisons are to be stored for later use, the profile is cooled and cut to the appropriate lengths.

Sheet - Extruded material over 0.254mm (0.01 in.) in thickness is classified as "sheet." Sheet extrusion is generally used for stock up to 6.35 mm (0.25 in.) in thickness. Polymers which are commercially extruded into sheet include ABS, acetal, LDPE, HDPE, LLDPE, HMWPE, EVA, polypropylene, polystyrene, and PVC.

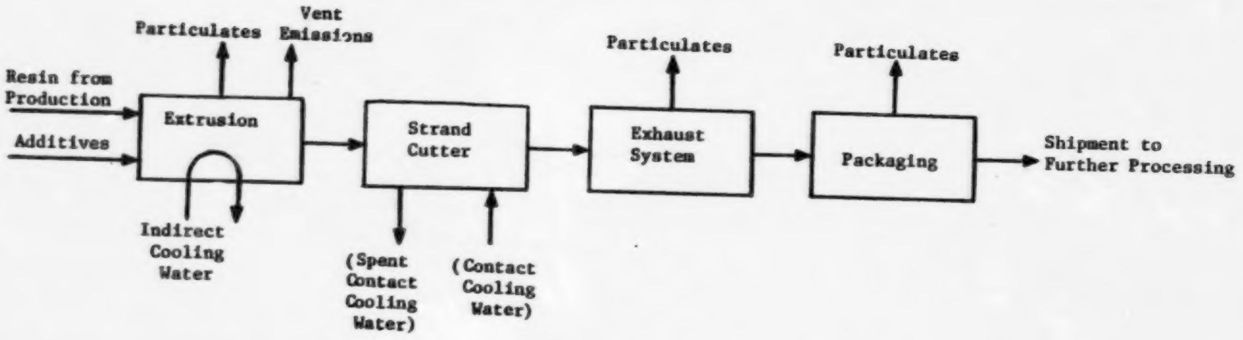
Particulates
Vent Emissions
Particulates
Particulates
Resin from Production
Additives
Extrusion
Strand Cutter
Exhaust System
Packaging
Shipment to Further Processing
Indirect Cooling Water
(Spent Contact Cooling Water)
(Contact Cooling Water)

Figure 25. Pelletizing.

Parentheses indicate that the stream is not present in all pelletizing operations.

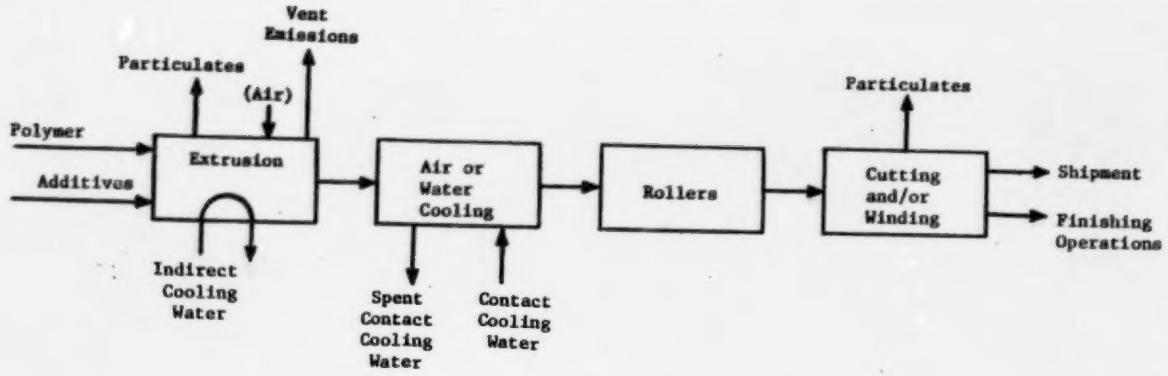
Polymer
Additives
Particulates
(Air)
Vent Emissions
Extrusion
Indirect Cooling Water
Air or Water Cooling
Spent Contact Cooling Water
Contact Cooling Water
Rollers
Particulates
Cutting and/or Winding
Shipment
Finishing Operations

Figure 26. Profile, pipe, and tube.

In sheet extrusion, the die extrudes a sheet of plastic directly onto water-cooled chrome-plated finishing rolls. The finishing rolls are often used to impart a surface texture to the sheet. They are also used to stretch the sheet when the rolls are run faster than the melt emerges from the die. Stretching orients the melt and is particularly necessary to avoid sagging during the heating of the sheet during thermoforming operations. Stretch ratios usually range from 3:1 to 4:1.[81] The hot plastic sheet may liberate some emissions until it is totally cooled.

A conveyor system carries the sheet to the rubber covered pull or nip rolls which run at the same surface speed as the finishing rolls. These feed the sheet to the cutting unit. The sheet is trimmed and cut to the specific product length and is then packaged or carried directly to thermoforming or finishing operations. Scrap plastic from trimming operations can be ground and recycled to the extruder feed. Cutting, packaging, and grinding operations can produce particulate emissions. A block diagram of sheet extrusion is shown in Figure 27. Typical sheet extruded applications include packaging materials, appliance housing, signs, and thermoforming input for luggage, boats, canoes, furniture, and refrigerator doors.

Film - Polymer film is commonly produced from fluoroplastics, polyester, LDPE, HDPE, HMWPE, EVA, polypropylene, polyurethene, and PVC by two different processes: flat film extrusion and blown film extrusion. Flat film extrusion follows the same process described for sheet extrusion except that the final film product is less than 0.254mm (0.01 in. thick).[120] It is usually wound onto storage rolls after leaving the pull rolls.

The most commonly blown film extruded polymers are LDPE and LLDPE. In blow extrusion the die extrudes a thin-walled hollow cylinder vertically upward. Air is forced into the hollow tube and expands the tube into a bubble of film with a thickness of less than 0.254 mm (0.01 in.). The blown film tube is usually six to seven times the diameter of the original extruded tube.[120] The tube is rapidly chilled by a blast of air from a circumferential chill ring. Guide rolls carry the film into the nip or pinch rolls at the top which squeeze the now solidified film together to form a double thickness. Guide rolls, which control the tension of the film, carry the film to be wound, slit, or cut to product specifications. Particulates may be generated during cutting operations. The film can also be sealed at intervals to produce plastic bags. The film then proceeds to shipment, finishing, and in some cases, thermoforming operations. A block diagram of blown film extrusion is shown in Figure 28. Typical blown film extrusion product applications include trash bags, food packaging, stretch wraps, liners, and covers.

Wire and Cable Coating - The plastic coating of wire and cable is a major use of extrusion. Typical polymers used in this operation include acetal copolymer, fluoroplastics, nylon 6/6, modified phenylene oxide, LDPE, HDPE, EVA, polypropylene, polyurethane, and PVC. Polymer melt is forced through a die which resembles that used for extruding tubing, except that the mandrel of the die is replaced by a tapered guide through which the wire or cable is fed. The wire or cable is preheated to the polymer melt temperature and the wire and polymer are extruded together as an integral unit. The coated wire or cable then passes through a water trough where it is cooled, thereby producing

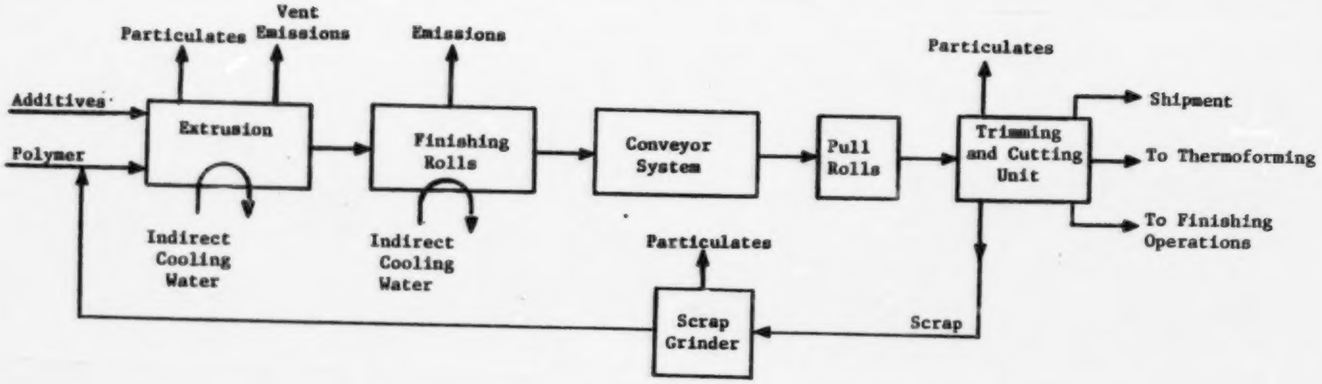
Additives
Polymer
Particulates
Vent Emissions
Extrusion
Indirect Cooling Water
Emissions
Finishing Rolls
Indirect Cooling Water
Conveyor System
Pull Rolls
Particulates
Trimming and Cutting Unit
Shipment
To Thermoforming
To Finishing Operations
Scrap
Particulates
Scrap Grinder

Figure 27. Sheet.

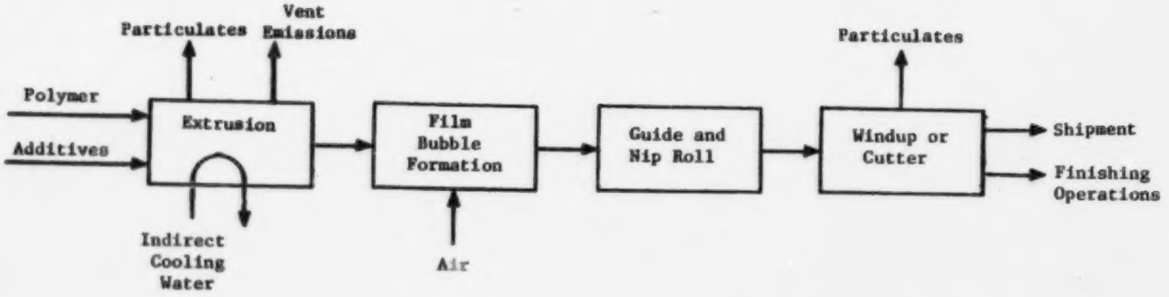
Particulates
Vent Emissions
Particulates
Polymer
Additives
Extrusion
Film Bubble Formation
Guide and Nip Roll
Windup or Cutter
Shipment
Finishing Operations
Indirect Cooling Water
Air

Figure 28. Blown film.

a cooling water waste stream. The tension is controlled by rolls as it is fed onto the wind-up drum.

The following table shows typical extruder output to be expected from wire coating with low density polyethylene.[22]

Extruder Size (mm)	Extruder Size (in.)	Output kg/hr
38	1.5	14
51	2	16-18
76	3	32-36
114	4.5	68-73
254	10	454-680

A block diagram of wire and cable coating is shown in Figure 29.

Coextruded (Multi-Layer) Products - The layered extrusion of several different polymers or several colors of the same polymer into single homogeneous profile, sheet, or film is termed coextrusion. Coextruded products are able to provide the best properties of several different polymers, thereby providing better product characteristics, such as chemical resistance, superior permeability, and/or lower composite cost.

A separate extruder system is set up for each polymer type and the systems are connected at a feed block which supplies the polymer melt to a single manifold die. The layers are extruded directly onto one another. The matrix illustrated in Figure 30 summarizes which polymers can be successfully coextruded with other polymers. The successfulness of the coextrusion is determined by the bond achieved between the layers. Permanent homogeneous bonds between two colors of the same polymer can be achieved. Some polymer combinations cannot be successfully achieved due to a chemical incompatibility between the additives normally used in the polymers. When it is desirable to join two such polymers, adhesive can be extruded as a layer between them.

After the layers are coextruded, they follow the post-extrusion processing steps for the shape that they most closely resemble (i.e., sheet, profile). Typical coextruded products include containers, packages, and disposal ware. A block diagram of the coextrusion segment is shown in Figure 31.

OPERATING PARAMETERS AND UTILITY REQUIREMENTS

The conditions under which extrusion operations are performed are strongly governed by the polymer being processed and the end product application. Most processors use company guidelines to determine rough settings for the temperature, pressure, and screw speed. The process is then fine-tuned by trial and error to determine the optimum operating temperature, pressure, and speed. Cooling and heating requirements are then determined to maintain the necessary operating parameters.

Some typical melt temperatures at the extrusion die are illustrated in Table 32 for commonly extruded polymers. Temperatures range from 175 to

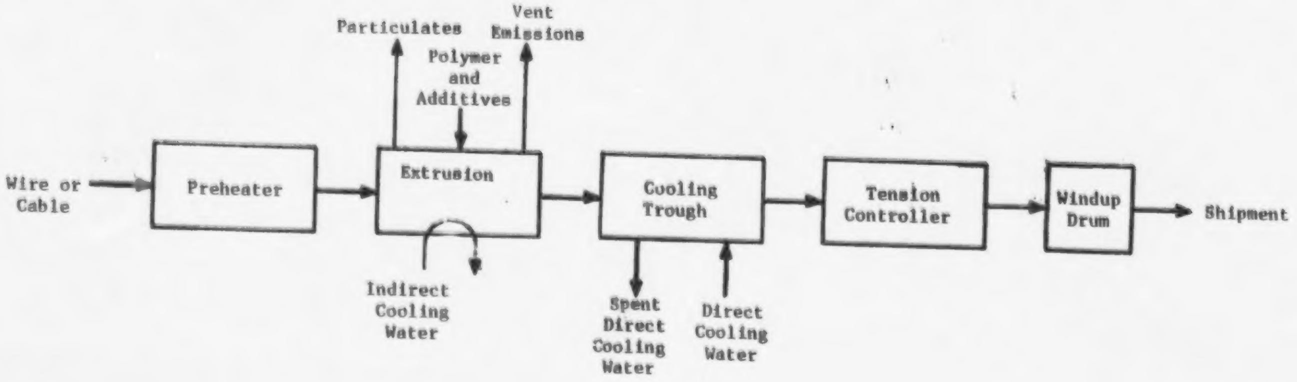
Particulates
Vent Emissions
Polymer and Additives
Wire or Cable
Preheater
Extrusion
Cooling Trough
Tension Controller
Windup Drum
Shipment
Indirect Cooling Water
Spent Direct Cooling Water
Direct Cooling Water

Figure 29. Wire and cable coating.

	Rigid PVC	Flexible PVC	ABS	Polyethylene	Polypropylene	EVA	Polystyrene
Rigid PVC		*	*	X	X	X	-
Flexible PVC	*		X	X	X	X	-
ABS	*	X		X	X	X	*
Polyethylene	X	X	X		*	*	*
Polypropylene	X	X	X	*		X	*
EVA	X	X	X	*	X		-
Polystyrene	-	-	*	*	-	-	

Legend: * - Coextrudable
X - Not Coextrudable
- - Coextrudabilty not found in the references

Figure 30. Coextrudability of commonly extruded polymers.

Sources: Beck, R. D., Plastics Product Design, 1980, p. 295.

DuBois, J. H. and F. W. John, Plastics, 1981, p. 126.

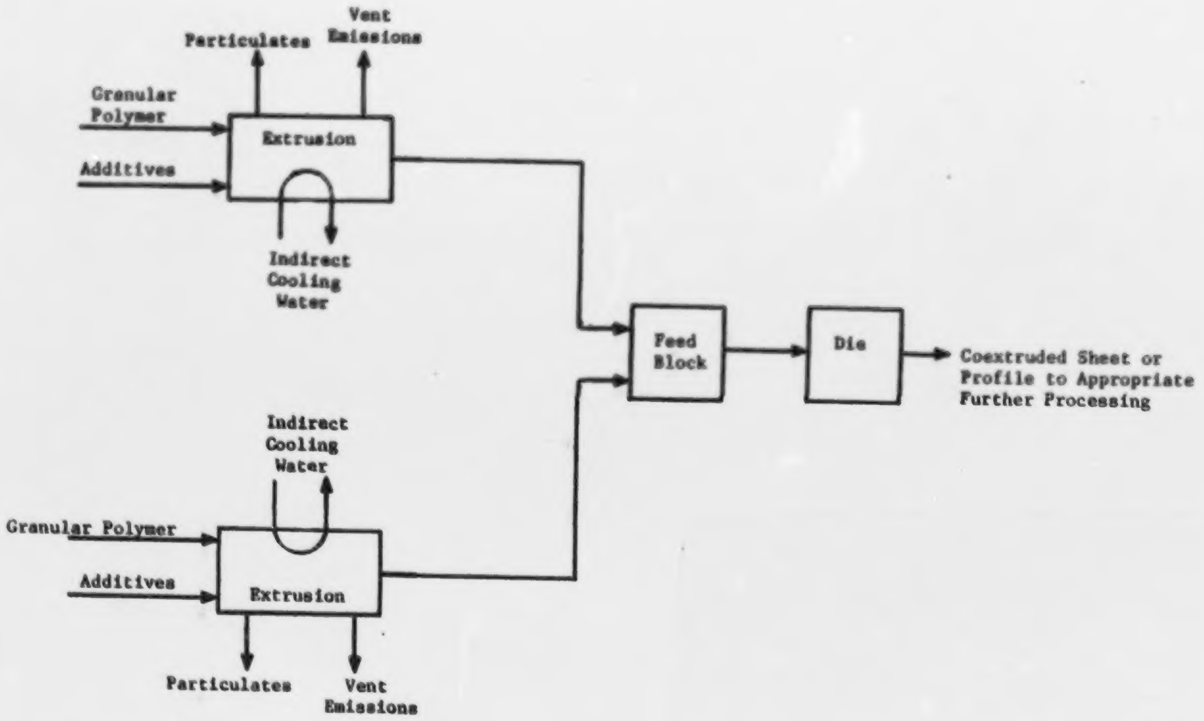
Particulates
Vent Emissions
Granular Polymer
Additives
Extrusion
Indirect Cooling Water
Feed Block
Die
Coextruded Sheet or Profile to Appropriate Further Processing
Indirect Cooling Water
Granular Polymer
Additives
Extrusion
Particulates
Vent Emissions

Figure 31. Coextruded (multi-layered products).

TABLE 32. EXTRUSION TEMPERATURES

Polymer	Melt Temperature at Die (°C)
Acrylic Resins	230
ABS	175 - 230
ABS/PVC Alloys	191 - 210
Fluoroplastics	260 - 330
Polyacetal	188 - 205
Polybutylene	130 - 190
Polycarbonate	250 - 300
Nylon	260 - 310
Polyester	
Thermoplastic	270 - 300
Aromatic	232 - 260
LLDPE	250 - 260
LDPE	150 - 178
HDPE	200 - 230
Polycarbonate	285 - 315
Polypropylene	200 - 230
Polystyrene	190 - 230
Polyurethane	150 - 200
PVC	190 - 210
SAN	175 - 225

Sources: Agranoff, J., Modern Plastics Encyclopedia, 1981-1982, pp. 4, 32, 49, and 100.

DuBois, J. H., and F. W. John, Plastics, 1981, p. 128.

Fisher, E. G., Extrusion of Plastics, 1976, p. 179.

Glanvill, A. B., The Plastics Engineer Data Book, 1973, p. 60.

Grayson, Martin (ed). Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Edition, (Vol:pp), 16:395, 466-467; 18:488.

Griff, A. L., Plastics Extrusion Technology, 1968, p. 69.

398°C. Table 33 illustrates typical extruder die head pressures for various extruded forms. Melt pressures range from 0.345 to 5.52 x 10^6 Pascal.

The power to turn the extruder screw is transmitted from the motor through gear drives. The extruder size, polymer melt rheology, and temperature determine the power requirements of each extrusion application. Table 34 shows the relationship between extruder size, power, and output.

The following table presents information pertaining to typical ranges of power requirements for some important polymers. The information on LDPE illustrates the different power requirements for various melt temperatures.

POWER REQUIREMENTS†

	KWh/kg/hr§
Polyolefins	0.2 - 0.3
Polycarbonate	0.14 - 0.22
PVC	0.15 - 0.2
LDPE - 170°C	0.14
200°C	0.16
230°C	0.19

†Source: Glanvill, A. B., The Plastics Engineer Data Book, 1973, p. 60.
§KWh required per kg output per hour operation.

WASTE STREAMS AND EMISSIONS

Extrusion operations produce air emissions, wastewater, and solid waste. Table 35 presents a summary of the point source emissions from extrusion operations. Particulates are formed by the storage, mixing, cutting, and trimming operations. Volatile emissions are released from the extruder cylinder and the exposed sheet surfaces. Wastewater is produced during product cooling. Cutting and trimming results in solid waste. Emissions and wastes are discussed in more detail in the text below. The Industry Description section of this document details the waste streams and emissions for major plastics additives used in extrusion.

Air Emissions - All extrusion operations have the potential to produce particulate and hydrocarbon emissions during the handling of the polymer and additives prior to and during processing. Resin and solid additive particulates are emitted from storage, blending, mixing, and grinding. Particulates are usually controlled by wet scrubbing.[177]

In most extruders, volatiles such as traces of unreacted monomer, additives, moisture, solvent from the polymerization process, or decomposition products need to be removed from the melt at some point along the cylinder axis. Decomposition products occur when excess heat causes the polymer to decompose. Table 36 presents those decomposition products which could be formed during extrusion along with the temperature above which it is likely to be formed. A cylinder vent is often connected to a vacuum system to remove these volatiles. The vacuum exhaust will contain volatile emissions.[160]

TABLE 33. EXTRUDER DIE HEAD PRESSURES

	Melt Pressure at Die (10^6 Pascal)
Monofilament	0.689 - 2.07
Sheet	0.345 - 1.03
Wire Coating	1.03 - 5.52
Pipe	0.345 - 1.03
Cast Film	0.345 - 1.03
Flat Film	1.38 - 4.14

Source: Glanvill, A. B., The Plastics Engineer Data Book, 1973, p. 60.

TABLE 34. TYPICAL EXTRUDER SIZES, OUTPUTS, AND DRIVE POWERS

Extruder Size			Output Capacity	Drive Power
(in.)	(mm)	L/D	kg/hr	kW
1 1/2	38.1	24:1	110-132	7.5-11.2
2	50.8	24:1	198-264	14.9-22.4
2 1/2	63.5	24:1	330-550	26.1-44.7
3 1/2	88.9	24:1	660-880	29.8-55.9
3 1/2	88.9	30:1	770-990	41.0-59.7
4 1/2	11.43	24:1	1,540-2,200	59.7-93.2
6	15.24	24:1	2,640-3,520	111.9-223.7
8	20.32	24:1	4,400-7,700	223.7-447.4

Sources: DuBois, J. H., and F. W. John, Plastics, 1981, p. 128.

Glanvill, A. B., The Plastics Engineer Data Book, 1973, p. 60.

Levy, S., Plastics Extrusion Technology Handbook, 1981, p. 29.

TABLE 35. EXTRUSION POINT SOURCE EMISSIONS

	Air Emissions							Waste-Water			Solid Waste		
	Particulates		Volatiles										
	Polymer	Additives	Monomer	Moisture	Additives	Solvent	Decomposition Products	Polymer	Plasticizer	Additives	Polymer	Plasticizer	Additives
Storage, Blending and Grinding	X	X											
Extruder			X	X	X	X	X						
Sheet Finishing Rolls			X										
Cooling								X	X	X			
Pelletizing, Cutting, and Trimming	X	X									X	X	X

TABLE 36. DECOMPOSITION PRODUCTS

Polymer	Highest Processing Temperature (°C)†	Decomposition Temperature (°C)§	Decomposition Products
Acrylic Resins	230	320	*
ABS	230	300	*
Fluoroplastics	330	300	HF
Nylons	310	300	CO, CO_2, NH_3, H_2O
Modified Phenylene Oxide	#	#	*
Polyacetal	205	250	*
Polybutylene	190	300	*
Polycarbonate	300	330	*
Polyester (Thermoplastic)	300	300	acetaldehyde
Polyester (Aromatic)	260	275	*
Polyethylene	230	100	Ketone carbonyl groups form due to oxidation
Polypropylene	230	300	*
Polystyrene	230	300	*
Polyurethane	200	300	*,##
PVC	210	100	HCl
Styrene Acrylonitrile	230	300	*

---

*Decomposition products are not formed at or near extrusion processing temperatures.

†This is the highest possible temperature reached by the normal extrusion of all formulations of the polymer listed.

§This is the lowest temperature at which decomposition products begin to form.

#Temperatures not found in the reference literature.

##The presence of humidity at processing temperatures may cause hydrolysis of the urethane functional groups.

Hydrocarbons from solvents and additives are generally removed by adsorption, incineration, or condensation.[177]

In addition to these emissions, pelletizing operations may produce particulates during cutting and packaging. The cutting and trimming of profile, pipe, tube, sheet, and film is also a potential source of particulate emissions, as is the grinding of scrap plastic. These particulates consist of fine particles of polymer and additives.

The extrusion of sheet and film exposes large surface areas as they are cooled and stretched. There is a tendency for some polymers to lose, by volatilization, a high percentage of residual monomer left in the polymer. These volatiles are in such low concentration that control would be difficult and with proper ventilation should present no problems.

Wastewater - Direct contact cooling water is produced during pelletizing operations when the extruded strands are submerged to facilitate cooling and cutting. Extruded profile, pipe, and tube are often cooled by a cooling water bath. Wire and cable is passed through a water trough to cool the product. These direct contact cooling water streams may contain soluble species and suspended polymer and additive particles from contact with the polymer.

Solid Waste - Thermoplastic scrap generated by post-extrusion trimming and cutting operations can usually be ground and recycled to the extruder feed. Excess scrap and particulates which cannot be recycled must be disposed of as solid waste. Since this waste is comprised of primarily inert plastic material, it will pose no hazardous disposal problems.

WORKER DISTRIBUTION AND EXPOSURE

Most extrusion process units are automated or semi-automated requiring fewer workers than such forming operations as compounding. We have estimated the number of workers per unit per shift by correlating equipment manhour requirements with the major pieces of equipment associated with the flow diagram shown in Figures 25 through 29 and 31. Employee distribution may vary slightly with the type of product extruded; for example, an operation in which product is pelletized following extrusion may require more employee attention than one in which sheet or profile is produced. Worker distribution estimates are shown below:

Unit	Workers/Unit/8-hour Shift
Mixing	0.5
Extrusion	0.5
Cutting/Trimming	0.25
Pelletizing	0.25
Scrap Grinding	0.25
Bagging/Packaging	1.0

Both process and fugitive emissions may be emitted from extrusion processes. Particulate and volatile emissions are possible. The compounds emitted will vary because of the wide variety of polymers typically extruded.

Potential workplace contaminants and release points have been estimated from information in the literature and are listed in Table 37. Toxicity information is summarized in Appendix C of this document and discussed in detail in IPPEU Chapters 10 and 10b.

Little data are available in the literature from which employee exposure potential in extrusion processes may be estimated. However, one source gives the following hydrocarbon emission factors for various resin types:

- Cellulosic--140 g/kg product
- HDPE--5.5 g/kg product
- LDPE--33 g/kg product
- Polyurethane--1 g/kg product
- PVC and copolymers--20-90 g/kg product
- PVC film only--6-24 g/kg product
- PVC sheet only--3-10 g/kg product

TABLE 37. EXTRUSION EMISSIONS AND RELEASE POINT ESTIMATION

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Storage, Mixing, Blending, Grinding	Fugitives	[1]Polymer Particulates - acrylics - ABS/SAN - engineering thermoplastics - fluoropolymers - polyamides - polybutylenes - polycarbonates - polyolefins - polystyrene - polyvinyl chloride - polyvinylidene chloride - polyethylene terephthalate - polybutyl terephthalate
		[2]Additive Particulates: Antioxidants - BHT - trisnonyl phosphite - dilauryl thiodipropionate
		Colorants - carbon black - titanium dioxide - Cd sulfoselenide - lead chromate - phthalocyanines - anthraquinone red - monoazo yellow

(continued)

TABLE 37 (continued)

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent	
Storage, Mixing, Blending, Grinding (continued)	Fugitives (continued)	**Flame Retardants**	- antimony oxide - alumina trihydrate - trixylenyl phosphate - decabromodiphenyl oxide - chlorinated paraffin wax
		Heat Stabilizers	- tribasic lead sulfate - Ba/Cd stearate - Ca/Zn stearate
		UV Stabilizers	- 2-hydroxy-4-octoxybenzophenone - 2 (2C-hydroxy-5' methylphenyl) benzotriazole - nickel dibutyldithio carbonate

(continued)

TABLE 37 (continued)

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Storage, Mixing, Blending, Grinding (continued)	Fugitives (continued)	**Plasticizers** - di-n-octyl phthalate - diisooctyl phthalate - diisodecyl phthalate - tricresyl phosphate - di (2-ethylhexyl) phthalate **Reinforcers** - glass fibers - asbestos - silica
	Mixing Machine, Materials Handling	Noise
Extruder	Barrel Vent, Extruder Die, Fugitives	[2]Volatile Additives - see above list. Volatile Solvent - VM & P naphtha [3]Volatile Monomers - methyl methacrylate - 1,3-butadiene - styrene - acrylonitrile - 2,6-xylenol - p-dichlorobenzene - chlorofluorocarbons

(continued)

TABLE 37 (continued)

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Extruder (continued)	Barrel Vent, Extruder Die, Fugitives (continued)	- formaldehyde - ethylene oxide - caprolactam - hexamethylenediamine - 1-butene - bisphenol-A - dimethylterephthalate - terephthalic acid - 1,4-butanediol - ethylene - 1-hexene - 1-octene - vinyl acetate - propylene - vinyl chloride - vinylidene chloride
		Decomposition Products - HF (fluoroplastics) - CO, CO_2, NH_3 (polyamides) - acetaldehyde (polyamides) - ketone carbonyls (polyethylene) - HCl (PVC)
Sheeting Finishing	Fugitives	[3]Volatile Monomer - see above list.

(continued)

TABLE 37 (continued)

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Pelletizing, Cutting, Trimming, Bagging	Fugitives	[1]Polymer Particulates [2]Additive Particulates
	Machining, Grinding	Noise

---

[1] Polymers typically extruded. Other polymers may be extruded for specialty applications.

[2] Specific additives listed are those documented in the literature. Many other additives may be used, depending on product coating applications.

[3] Primary monomers used to produce the plastics typically extruded. Other monomers or comonomers may also be present.

SECTION 7

FINISHING OPERATIONS

FUNCTION

Parts produced by the plastics processing steps described in this document are turned into consumer products by a variety of finishing operations. Finishing operations render the plastic parts useful by way of processes which can be categorized as follows:

- Machining
  Drilling, Sawing
- Decorating
  Painting, Printing, Hot Stamping,
  Vacuum Metalizing, Electroplating
- Assembling
  Solvent Welding, Ultrasonic Welding,
  Electronic Heat Sealing, Hot Gas Welding

The series of finishing operations which each plastic part undergoes is specifically designed for the efficient production of a useful consumer product.

The finishing of plastic products can be carried out either by the machine operators immediately after the part has been produced or as a function of a separate department. The two major factors which influence the location of equipment for finishing operations are the production rate of the machine and the number of finishing operations required.[136]

Product flash removal and simple trimming are most commonly performed immediately after processing. These operations are shown in each plastic processing operation where they are employed. This section focuses on the finishing operations which are performed after the initial flash removal and simple trimming operations are completed.

INPUT MATERIALS AND END PRODUCTS

The input materials to finishing operations are the products produced by all of the plastics processing operations previously discussed in this document. Other input materials include paints, screws, printed foils, adhesives and other materials required to finish the product. The end products of finishing operations are the finished plastic products ready for consumer or industrial use. Table 38 presents a summary of the input materials and end products for each type of finishing operation.

PROCESS DESCRIPTION

Finishing operations cover a wide range of different operations which will be discussed in this section in three areas: Machining, Decorating, and Assembling. Depending upon the product specifications, parts may undergo operations in one or all of these areas.

Machining

Machining operations are used to drill, cut, mill and otherwise shape products from plastic processing operations to match final product specifications. Plastic materials can usually be machined using conventional machining equipment. It is most important that machining operations performed on plastics use sharp tools and avoid over-heating. The drilling and cutting specifications such as drill or blade type and speed must be specifically determined for each polymer formulation. They must be chosen to minimize heat generation particularly for thermally sensitive resins such as PVC, acetal, polystyrene, polycarbonate, and cast thermoset resins.[72] Efficient cooling is essential to successful machining operations. Air or cutting oil in liquid or vapor spray are most frequently used. Carbon dioxide (CO_2) jets are often used as coolant when machining thermoplastics to prevent them from melting.

Decorating

Plastic parts are decorated for aesthetic and functional purposes. Decorative finishes are applied to plastic parts by a variety of methods including painting, printing, hot stamping, vacuum metallizing, and electroplating. Laminating and coating can be used to finish sheet products particularly to achieve color and surface finish. These operations and how they are used for product finishing are discussed in detail in the Coating and Laminating sections of this document (Sections 4 and 12).

Painting of plastic parts is most commonly performed by spray painting. Either enamels or lacquers are used. Enamels usually require heating to cure them and lacquers dry at room temperature by solvent evaporation. Various types of spray masks are used to allow designs and multiple colors to be printed on the plastic parts.

Dip coating is sometimes used to economically paint the entire surface of parts. The parts are lowered into a tank of lacquer, withdrawn and allowed to dry. When raised areas have been molded into the plastic product, decorating is often performed by roller coating or spray and wipe. Roller coating involves coating a roller with paint and rolling it over the raised surfaces of the part. In this way only the raised areas are decorated. The reverse effect is created by the spray and wipe technique. The entire part surface is sprayed with paint and the paint is wiped off of the raised surfaces leaving paint only in the mold recesses.

TABLE 38. FINISHING OPERATIONS SUMMARY

Finishing Operation	Type of Part	Typical Product Types
MACHINING		
Sawing and Drilling	Thermoplastic and thermoset parts and sheets	Wide variety of products
DECORATING		
Painting	Lacquers: Acrylic Polystyrene Enamels: Phenolic Nylon Enamels or Lacquers: ABS Acetals Polycarbonate Polyethylene Polypropylene Polyvinyl Chloride Polyester	Wide variety of products
Printing-Silk Screening	Thermoplastic and thermoset parts and sheets	Wide variety of products
Hot Stamping	Thermoplastic and thermoset parts and sheets	Wide variety of products
Vacuum Metallizing	ABS Phenolic Polycarbonate Polyester Polystyrene	Appliance parts Decorative automotive parts Housewares Toys and novelties
Electroplating	ABS Acetal Phenolic Polycarbonate Urea formaldehyde	Automotive parts Door handles Housewares Nameplates Plumbing parts

(continued)

TABLE 38 (continued)

Finishing Operation	Type of Part	Typical Product Types
ASSEMBLING		
Solvent Welding	Thermoplastic and thermoset parts	Wide variety of products
Ultrasonic Welding	Thermoplastic parts	Flashcubes Ballpoint pens Toys Housewares
High Frequency Electronic Welding	ABS Polyvinyl chloride	Air mattresses Chaise lounge pads Water beds Inflatable toys Cushions Flotation devices Mattress pads Automotive upholstery
Hot Gas Welding	Polyvinyl chloride Polyethylene Polypropylene	Wide variety of products
Spin Welding	Thermoplastic parts	Dual colored knobs Insulated drink cups Bottle halves Lamp gloves
Thermal Heat Sealing	Polyethylene Polypropylene Polyvinyl chloride	Pipe sections Pipe fittings Flanges

Sources: Baird, R. J., Industrial Plastics, 1971, pp. 249-261.

Beck, R. D., Plastic Product Design, 1980, pp. 287-299.

Dubois, J. H. and F. W. John, Plastics, 1981, pp. 203-225.

Milby, R. V., Plastics Technology, 1973, pp. 220-225 and pp. 445-453.

Printing of plastic parts is most frequently performed by silk screen decorating. In this process paint or ink is forced through a stencil fabric onto the area of the plastic part which is to be decorated. The stencil fabric is generally made of nylon or perforated stainless steel. It is placed on top of the part and a squeegee forces the paint through the screen openings and onto the plastic. A series of different screens with various colors of paints can produce intricate multi-colored patterns.

Polymer sheets produced from calendering, casting, and extrusion operations can be printed by a number of methods such as rotogravure, silk screen, spanishing, and tipping. These operations usually occur immediately after the sheet production process. Most commercial printing is performed by the rotogravure method which applies the color by patterned rollers. Spanishing involves depositing ink in the hollows of an embossed sheet. Tipping involves applying ink to the tops of the embossing by an engraved roller.[61]

Hot Stamping of plastics is performed to mark and decorate the surface of plastic parts. It is one of the most popular decorating techniques used in the industry. Hot stamping consists of transferring a design or pattern from a thin polyester or cellophane film (called a foil) onto a plastic part. Most plastics can be decorated by hot stamping.

The hot stamping foil is comprised of a pigment or metal coating on the carrier film. Foils of this type are available in a variety of colors and types for specific resin formulations and product applications from foil manufacturers. The foil design is transferred to the plastic part by way of heat and pressure. Designs are applied by the use of heated rollers or dies. As pressure is applied, the coating on the foil transfers from the film to the plastic surface and fuses in place.

Vacuum Metallizing of plastics provides a bright, attractive, metallic appearance to parts by coating the plastic with a thin layer of metal. Such parts are light weight and can withstand moderate wear. Most plastics can be satisfactorily vacuum coated although polystyrene, polyester, polycarbonate, phenolic, and ABS are most frequently used.

A block diagram of the vacuum metallizing process is shown in Figure 32. The plastic parts are first coated with a base coat of lacquer by spraying. Occasionally parts are coated by dipping. This evens out any surface defects. The parts are then oven dried and placed on rotating carriages. The carriages have tungsten wire filaments connected to pieces of aluminum wire. After the carriages are placed in a vacuum chamber, heat from the tungsten filaments vaporizes the aluminum wire. The aluminum molecules condense on the surface of the cool plastic parts resulting in the final product.

Typical vacuum metallized products include plated housewares such as candlesticks and salt and pepper shakers, appliance cabinets, decorative automotive dash panels, and plated polystyrene toy parts.

Electroplating of plastics is used to produce parts which have the advantages of lightweight plastic parts yet work well in metallic applications. Commonly electroplated plastics include ABS, acetal, polycarbonate, phenolic, and urea formaldehyde.

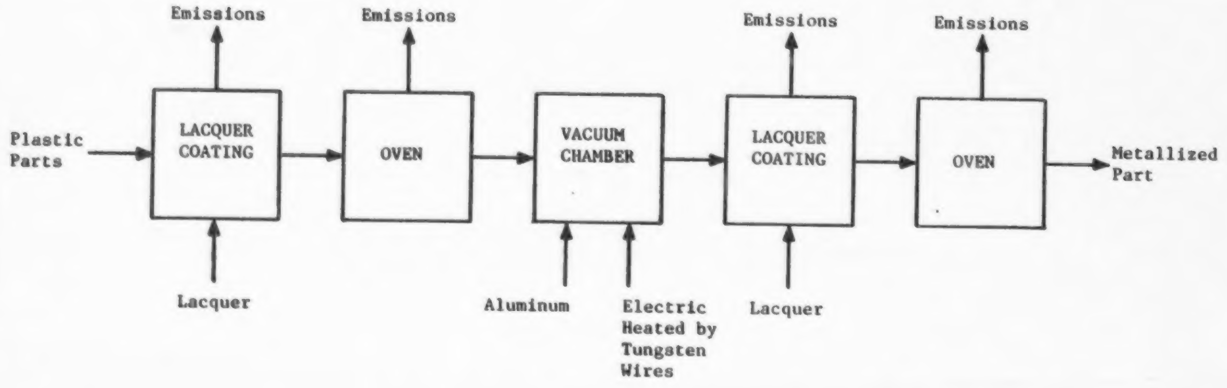
Emissions
Emissions
Emissions
Emissions
Plastic Parts
LACQUER COATING
OVEN
VACUUM CHAMBER
LACQUER COATING
OVEN
Metallized Part
Lacquer
Aluminum
Electric Heated by Tungsten Wires
Lacquer

Figure 32. Vacuum metallizing.

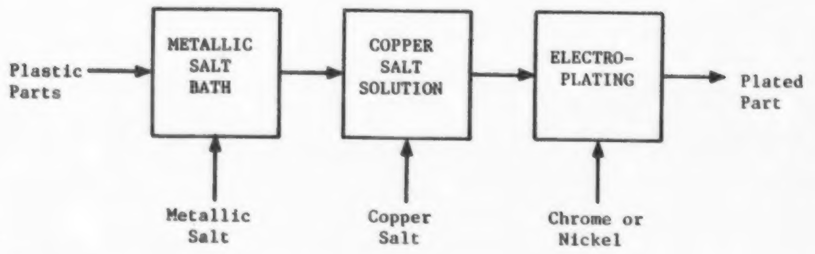
Plastic Parts
METALLIC SALT BATH
COPPER SALT SOLUTION
ELECTRO-PLATING
Plated Part
Metallic Salt
Copper Salt
Chrome or Nickel

Figure 33. Electroplating.

A block diagram of electroplating is shown in Figure 33. During the electroplating process the plastic part is first coated with a conductive film, usually copper. The part is immersed in a bath containing a metal salt. It is then immersed in a copper salt solution. The part is then plated with either chrome or nickel.

Electroplated products are particularly useful in the plumbing industry and in the production of small appliances. Typical applications include housewares, plumbing parts, tail lamp housings, automotive grills, door handles, and name plates.

Assembling

Assembling involves the joining of two or more plastic parts into the final product design. Multiple assembly parts are typically toys, appliances, and electronic circuitry. Typical assembly methods include adhesive bonding, solvent welding, ultrasonic welding, high frequency electronic welding, hot gas welding, spin welding, and thermal heat sealing.

Adhesive bonding is one of the simplest methods of joining two plastic parts together. It involves applying an adhesive on one or both surfaces to be bonded and joining those surfaces together. The adhesive connects the two plastic parts but does not join the plastics on a molecular level.

Solvent welding involves using solvents to join two plastic surfaces together. The surfaces are either soaked in solvent and immediately brought together or solvent guns are used to inject solvents between adjacent surfaces.

Ultrasonic welding is used to join rigid thermoplastics such as ABS, acetal, polycarbonate, and polystyrene. Typical products joined by ultrasonic welding are flash cubes, ballpoint pens, toys, and housewares. During ultrasonic welding, the molecules located on the surface of the plastic are sufficiently disturbed by ultra-high frequency mechanical energy to create frictional heat. Such heat causes the plastics to melt and weld together in a fraction of a second.

High frequency electronic welding (HF) is performed primarily on polyvinyl chloride and ABS sheets and films. Aluminum or brass dies transmit electrical impulses to the thermoplastic which causes the molecules of the plastic to rotate about the dipole moment. The heat generated is sufficient to cause the plastic surfaces to melt and fuse. HF sealing forms a strong weld and is often used during the finishing of air mattresses, water beds, inflatable toys, cushions, flotation devices, and automotive upholstery.

Hot gas welding consists of directing a hot gas to the joint area of two plastic parts, causing the plastic to melt and fuse. This process is most commonly used with polyvinyl chloride, polyethylene, and polypropylene. The hot gas is either air or an inert gas such as nitrogen. Gas temperatures range from 204 to 316°C (400 to 600°F).[59]

Spin welding or friction welding is used to join thermoplastic parts having circular configurations. The parts to be welded are rotated against each other. Most frequently, one element is rotated and the other remains stationary. The heat generated by the friction between the two causes the plastic to melt. When the rotation ceases, a weld is formed between the part surfaces.

Thermal heat sealing is used to join thermoplastic parts which cannot be attached by solvent welding, ultrasonic welding, or spin welding techniques. This method is particularly useful for polyethylene, polypropylene, and polyvinyl chloride. The plastic surfaces to be joined are brought in contact with a hot plate. They are held there briefly to melt the plastic and are then quickly joined together in a wringing motion. Thermal heat sealing is frequently used for pipe sections, fittings, and flanges.

OPERATING PARAMETERS AND UTILITY REQUIREMENTS

The operating parameters used for each finishing operation are uniquely determined by the product specifications. Machining operations are performed at ambient temperatures and pressures. Special care must be taken to prevent excessive heating of the plastic due to the friction created by drilling and sawing. Drill bits and saw blades are specifically chosen to dissipate frictional heat. Table 39 presents a summary of the machining properties and operating parameters for a number of frequently encountered polymers.

Decorating operations which involve painting and printing are performed at ambient pressures and temperatures. When enamels are used, the part is often baked after painting. Typical baking temperatures range from 65 to 149°C (150 to 300°F).[15] Hot stamping operations are generally performed with the die surface around 93°C (200°F).[10]

Welding operations are performed at ambient pressure. Temperatures must be determined individually for each polymer and application in which welding is involved.

WASTE STREAMS AND EMISSIONS

Finishing operations produce air emissions, wastewater, and solid waste. Finishing operations are generally performed in a separate location from polymer processing operations and therefore these wastes may or may not be combined with the polymer processing wastes. Table 40 presents a summary of the point source emissions from finishing operations. Emissions and wastes are discussed in more detail in the text below.

Air Emissions - Finishing operations can generate particulates and volatile emissions. Particulates are generated during the machining operations. These particulates consist of fine particles of polymer, plasticizer, pigments, fillers, and other additives. Volatile emissions are released during the use of paints and solvents in the decorating and joining operations. Some monomer and additives may also be volatilized during annealing and enamel baking. Temperatures reached during finishing operations are not high enough to generate decomposition products.

TABLE 39. TYPICAL MACHINING PROPERTIES AND PARAMETERS

Polymer	Machining Properties	DRILLING	CIRCULAR SAW		BAND SAW	
		Drill Speed (rpm)	Blade Type	Speed (M per min)	Blade Type	Speed (M per min)
Acetal	Excellent	300 - 800	Hollow Ground	2,438	Metal	457
Acrylic	Good	1,500 - 2,500	Hollow Ground	914	Metal	609 - 1,219
Acrylonitrile-Butadiene-Styrene	Good to Excellent	500 - 900	Combination	1,219	Wood-Skiptooth	305 - 914
Diallyl Phthalate	Fair	600 - 2,000	Carbide Tip	609	Metal	609
Epoxy	Fair	500 - 1,000	Carbide Tip	914	Metal	457
Fluoroplastics	Excellent	1,000 - 2,000	Hollow Ground	2,438	Wood-Skiptooth	366 - 457
Melamine Formaldehyde	Fair	600 - 2,000	Hollow Ground	1,524	Metal	609
Nylon	Excellent	900 - 1,500	Hollow Ground	1,524	Wood-Skiptooth	305
Phenol Formaldehyde	Fair to Good	600 - 2,000	Carbide Tip	914	Metal	457
Polycarbonate	Excellent	300 - 800	Hollow Ground	2,438	Metal	457
Polyester	Good	500 - 2,000	Carbide Tip	1,524	Metal	1,219
Polyethylene LD	Good	1,000 - 3,000	Hollow Ground	2,743	Wood-Skiptooth	366 - 457
Polyethylene HD	Excellent	1,000 - 3,000	Hollow Ground	2,743	Wood-Skiptooth	366 - 457
Polyphenylene Oxide	Excellent	500 - 900	Hollow Ground	1,524	Wood-Skiptooth	609 - 914
Polypropylene	Good	1,000 - 3,000	Hollow Ground	2,743	Wood-Skiptooth	366 - 457
Polystyrene	Good	1,500 - 2,500	Hollow Ground	609	Metal	914 - 1,219
Polysulfone	Excellent	1,000 - 2,500	Hollow Ground	914	Metal	609 - 914
Polyurethane	Fair to Excellent	1,000 - 3,000	Hollow Ground	1,219	Wood-Skiptooth	305 - 609
Polyvinyl Chloride	Excellent	900 - 2,000	Hollow Ground	914	Metal	609 - 914

Sources: Baird, R. J., Industrial Plastics, 1971, pp. 274-275.

Glanvill, A. B., The Plastics Engineer Data Book, 1973, pp. 142-151.

TABLE 40. FINISHING OPERATIONS POINT SOURCE EMISSIONS

	Air Emissions							Waste-water		Solid Wastes			
	Particulates				Volatiles								
	Polymer	Plasticizer	Additives	Fillers	Monomer	Additives	Paints and Solvents	Polymer	Additives	Polymer	Plasticizer	Additives	Fillers
MACHINING													
Drilling and Sawing	X	X	X	X				X	X	X	X	X	X
DECORATING													
Painting							X						
Printing							X						
Hot Foil Stamping													
Vacuum Metallizing													
Electroplating													
JOINING													
Welding Methods					X	X							
Solvent Welding					X	X	X						

Wastewater - Water is often used as a cooling medium during machining operations. Such water will contain polymer and additive particles.

Solid Waste - Machining operations generate solid waste from the drilling and sawing of plastic parts. Depending upon the processing operation, these particulates may be recycled to the polymer feed of the processing operation.

WORKER DISTRIBUTION AND EXPOSURE

Finishing operations for plastics and resins require varying degrees of manpower commitment. Most are at least semi-automated. Some, like electroplating, may be fully automated. Estimates of worker distribution for major finishing operations are given below:

Unit (Operation)	Workers/Unit/8-hour Shift
Machining	0.5
Decorating/Coating/Painting	0.5 - 1.0*
Vacuum Metallizing	0.5
Hot Stamping	0.5
Electroplating	0.5
Assembly	0.5 - 1.0*

*Depends on degree of process automation.

The primary employee exposure concern from finishing operations is particulate emissions from machining. Polymer, plasticizer, colorant and other additive particulates may be released when formed products are machine-finished. Employees also may be exposed to inert gases (principally carbon dioxide) used to cool thermally sensitive resin parts.

Employees assigned to painting operations may be exposed to lead and hexavalent chromium as well as toluene, xylene or methyl ethyl ketone used as a solvent. Solvents typically used in printing or silk screening include methyl ethyl ketone, methyl isobutyl ketone and isophorone. Employees involved in this finishing operation may also be exposed to a multitude of inks, dyes, and dye solvents.

Exposures from electroplating operations include heavy metal salts (e.g. nickel, chromium, tin, cadmium) from mixing plating baths, hexavalent chromium and sulfuric, nitric, hydrocloric or phosphoric acid mists.

Assembly operations present potential exposures ranging from solvents used in adhesives and solvent welding to inert gases used in hot gas welding to non-ionizing radiation (radio frequency or microwaves) used in ultrasonic and high frequency welding. Small amounts of residual monomer may be present if welding operations produce temperatures approaching the volatilization point.

Good industrial hygiene practice dictates that employee exposure at individual plants must be determined through employee monitoring, which is discussed in Section 1 of this document.

FOAM

Foamed plastics (often called cellular or expanded plastics) are made by adding a gas to thermoplastics or thermosets, in order to form a spongelike material. Plastic foam production has become one of the major processing techniques of the plastics industry and has wide commercial use in the areas of flotation, packaging, cushioning, and insulation. Plastic foams are competing directly with wood, metal, paper, and glass applications. Polyurethane foams comprise the largest share of the polymer foam market although applications for polystyrene, polyethylene, polypropylene, polyvinyl chloride, phenolic, and epoxy are growing fast.

Plastic foams can be classified as rigid (resistant to crushing) or flexible (easily crushed). Foams with interconnected cells or openings have an open cell structure which allows liquid to pass through and they are usually flexible. Foams with closed cell structures have separate air or gas filled cells, are usually rigid, and will not allow liquid to pass.

The production of foamed plastic products will be discussed in this section in four process descriptions:

- Expandable Bead Foams,
- Extruded Thermoplastic Foams,
- Multicomponent Thermoset Foams, and
- Structural Foams.

SECTION 8

EXPANDABLE BEAD FOAMS

FUNCTION

Expandable bead foam is a closed-cell, rigid plastic foam material characterized by fused polymer spheres. Such foam is manufactured from spheres impregnated with an expanding agent which causes the beads to puff and fuse when exposed to heat. Expandable bead foams can have bulk densities which range from 16 to 80 kg/m^3 (1 to 5 lbs/ft^3).[60]

Expandable bead foams provide a unique combination of low material cost, zero water absorption, rigidity, impact resistance, shock absorption, and thermal insulation. These foams have found market applications in the areas of packaging, insulation, and flotation.

INPUT MATERIALS AND END PRODUCTS

The input materials for expandable bead foam production are tiny beads or spherical particles which have been impregnated with a hydrocarbon. The only polymers commercially used for this process are polystyrene and polyvinyl chloride (PVC). Polystyrene comprises the bulk of expandable bead foam products which are produced, and PVC is used primarily for thermal insulation applications.

Polystyrene beads are produced by polymerizing styrene in a water suspension to which a volatile liquid such as n-pentane has been added. As the polymer forms, the volatile agent is surrounded by the polymer to form spherical, gas-filled beads. The raw material has a typical bulk density of approximately 641 kg/m^3 (40 lb/ft^3) and contains from 5.5 to 7.4 percent blowing agents.[221] All compounding is performed during the production of the expandable beads and the molder commonly utilizes the beads as received from the producer.

The raw material is usually purchased by the foam processor in drums or rail car lots. Depending upon the intended product requirements, the foam processor can select beads in a range of sizes (0.197 to 1.475 cm^3).[136] Although they are most commonly purchased and used in their natural white color, the beads may be purchased in a variety of colors.

Prior to use, the beads are stored below 21°C (70°F) to inhibit the volatile agent from prematurely expanding the beads.[175]

Expandable bead foams are used for packaging and protecting products, flotation devices, insulation in construction and refrigeration, and hot and cold containers. Table 41 presents a list of typical products produced by the expandable bead foam process.

PROCESS DESCRIPTION

Unlike input materials to most other processes, expandable beads do not require formulation prior to processing since all formulation occurs during the bead production. As shown in Figure 34, polystyrene beads are usually pre-expanded to a bulk density close to the desired product bulk density in order that further processing can be performed more efficiently. The bead is expanded up to as much as 40 times the original volume during pre-expansion.

Pre-expansion is performed in batch or continuous operations. Pre-expansion equipment commonly consists of a steam chamber with baffles and mechanical agitation. The pre-expansion step requires short residence times, normally on the order of a few minutes.

After pre-expansion, the beads are usually dried and transported on a fluidized bed conveyor to storage where they are allowed to cool. The storage silos are constructed of large mesh bags.[221] The beads remain in storage for at least 5 to 36 hours in order to allow the beads to age. As the expanded beads cool, the blowing agent, still trapped inside the bead, condenses, thereby creating a pressure gradient across the bead wall. Aging allows the trapped pressure to equilibriate, assures that any residual liquids have evaporated, and allows the beads to cool and become hard. The storage of pre-expanded polystyrene beads poses a fire hazard created by their liberation of volatile gases, their susceptability to retain static charge, and the flammability of polystyrene. The expanded beads can be stored for as long as a few weeks before final molding.

The expanded beads are fed to molding operations either pneumatically or by gravity. A premeasured amount of beads are fed to a preheated split cavity mold. Aluminum molds are commonly used, although brass and stainless steel are also employed. Metals allow the proper heat transfer for heating and cooling operations. Steam is supplied to the mold cavity through small holes in the mold. The heat supplied by the steam causes the impregnated beads to expand to fill the confines of the mold. The soft and molten bead skins fuse together to form a single polymer mass. After expansion is completed, the mold and part are water cooled by water circulation through the mold cooling channels. The water contacts the part through the steam holes. The mold is then opened and the cooled foam part is ejected either by air pressure, mechanical pins, or manually. Parts are then trimmed and finished according to product designs.

Expandable beads can be extruded into film or sheet using extruders under carefully controlled conditions. Thin foam films with a satin-like sheen are most often produced for use in coasters, food tray liners, and wrapping materials. Extrusion of expandable beads is not a widely used process since the economics for this type of extrusion are unfavorable as compared with

TABLE 41. EXPANDABLE BEAD FOAM END PRODUCTS

Polymer	Product
Polystyrene	Display racks
	Foam slabs and blocks
	Flotation items: buoys pontoons life belts
	Liners: foundation roof deck
	Marine applications
	Novelties and toys
	Shipping and packaging containers
	Thermal insulation: cool storage warehouse insulation truck insulation hot disposable cups hot and cold liquid containers picnic coolers refrigerator and freezer liners
Polyvinyl Chloride	Thermal insulation applications: cool storage insulation warehouse insulation truck insulation

Sources: Dym, J. B., Injection Molds and Molding, 1979, p. 322.

Rodriguez, F., Principles of Polymer Systems, 1970, p. 362.

Wiman, J. V., "Expandable Polystyrene Molding," Modern Plastics Encyclopedia 1981-1982, 1981, p. 296.

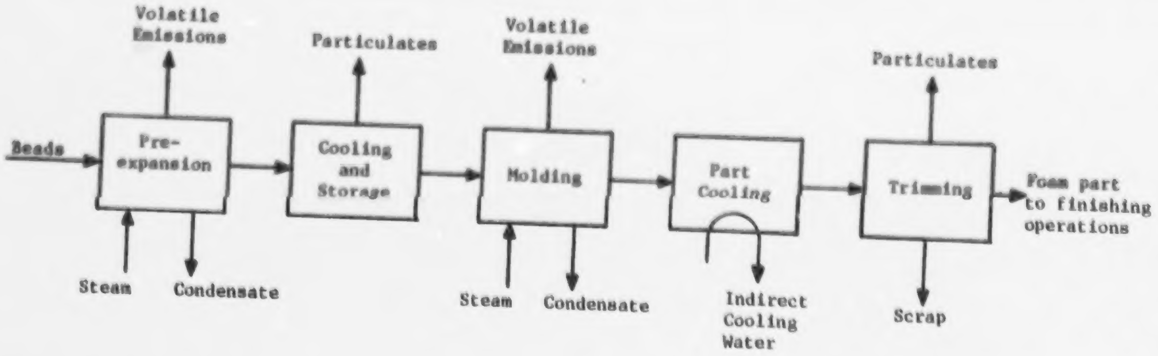
Volatile Emissions
Particulates
Volatile Emissions
Particulates
Beads
Pre-expansion
Cooling and Storage
Molding
Part Cooling
Trimming
Foam part to finishing operations
Steam
Condensate
Steam
Condensate
Indirect Cooling Water
Scrap

Figure 34. Expandable bead foams.

conventional extruded foams due to low output rates and the high equipment cost of the extruder system.

OPERATING PARAMETERS AND UTILITY REQUIREMENTS

The conditions under which expandable bead foam operations are performed are governed by the product design and shape. Table 42 presents typical temperatures, pressures, and cycle times for the bead foam molding process. Typical total cycle times range from 40 seconds to four minutes depending upon the part configuration, wall thickness, and foam bulk density.[221]

Low pressure steam is required during the bead pre-expansion, mold preheating, and molding process steps of the process. Steam flow requirements are determined by the process temperatures. Cooling water is required for cooling operations.

WASTE STREAMS AND EMISSIONS

Expandable bead foam operations produce air emissions, wastewater, and solid waste. Table 43 presents a summary of the point source emissions from expandable bead foam production.

Air Emissions - Expandable bead foam operations produce particulate and volatile air emissions. Particulates are formed during the cooling, storage, and transfer of pre-expanded beads as well as during the trimming of molded foam parts. When trim scrap is ground and recycled, grinding and transfer operations also produce particulates. Particulates are comprised of polymer and additive particles.

Volatile emissions are liberated from the pre-expansion and molding process steps. Such emissions contain volatilized monomer, released expansion agent, steam, and decomposition products. Decomposition products occur when excess heat causes the polymer to begin to decompose. Table 44 presents those decomposition products which could be formed during expandable bead foam molding.

Wastewater - Cooling water, which circulates through the mold chambers, contacts the foam product through the steam holes. Such water will contain dissolved volatiles, polymer, and additive particles and is usually recycled.

Solid Waste - Bead foam scrap is produced by the trimming of molded parts and from the collection of particulates. Such waste can sometimes be ground and recycled as filler to non-critical end uses such as large foam blocks and slabs. Excess scrap and particulates which cannot be recycled must be disposed of as solid waste.

Problems may be presented by the disposal of polystyrene and polyvinyl chloride wastes. Polystyrene and styrene have reportedly caused tumors in testing on animals conducted and reported by NIOSH.[107,108] PVC formulations commonly contain di-(2-ethyl-hexyl) phthalate (DEHP). DEHP is currently suspect as a carcinogen as a result of test data which indicates that it may cause cancer in rats.[160]

TABLE 42. EXPANDABLE BEAD FOAM OPERATING PARAMETERS

Process Step	Temperature °C	Pressure	Cycle Time
Pre-expansion	79° to 96°	Atmospheric	1 - 5 min.
Bead Storage	below 27°	Atmospheric	min. 5 hours
Mold Preheat	a	Atmospheric	10 - 30 sec.
Foam Molding	110° to 116°	18 to 30 psi	5 - 11 sec.
Cooling	79° to 96°	18 to 30 psi	2 - 8 min.

---

[a] Temperature not available in the reference literature.

Sources: Milby, R. V., Plastics Technology, 1973, p. 255.

Rodriquez, F., Principles of Polymer Science, 1970, p. 362.

Wiman, J. V., "Expandable Polystyrene Molding," Modern Plastics Encyclopedia, 1981-1982, p. 296.

TABLE 43. EXPANDABLE BEAD FOAM POINT SOURCE EMISSIONS

	Air Emissions						Waste-water		Solid Waste	
	Partic-ulates		Volatiles							
	Polymer	Additives	Monomer	Decomposition Products	Expansion Agent	Steam	Polymer	Additives	Polymer	Additives
Pre-expansion			X	X	X	X	X	X		
Cooling/Storage	X	X							X	X
Molding			X	X	X	X	X	X		
Trimming	X	X							X	X

TABLE 44. DECOMPOSITION PRODUCTS

Polymer	Highest Processing Temperature (°C)†	Decomposition Temperature (°C)§	Decomposition Products
Polystyrene	116	300	*
Polyvinyl Chloride	116	100	HCl

---

*Decomposition products are not formed at or near expandable bead foam processing temperatures.

†This is the highest possible temperature reached by expandable bead foam operations.

§This is the lowest temperature at which decomposition products begin to form.

WORKER DISTRIBUTION AND EXPOSURE

Expandable bead foams are produced via either batch or continuous process. More employee time is required for batch operation than for continuous operation. We have estimated worker distribution for expandable bead foam production by correlating major equipment manhour requirements with the process flow diagram in Figure 34. Estimates are shown below:

Unit	Workers/Unit/8-hour Shift
Pre-expansion	0.5 - 1.0*
Storage/Transport	0.5
Molding	0.5
Trimming/Finishing	0.5

*Larger requirement for batch processing.

Polyvinyl chloride and polystyrene polymers used in expandable bead foams are formulated during polymerization, thus eliminating the potential for employee exposure to particulate emissions during mixing and blending. However, employees may be exposed to both particulate and gaseous emissions from each processing step.

Substances potentially present in the workplace are listed with probable release points in Table 45. Toxicity information is provided in Appendix C of this document and in IPPEU Chapters 10 and 10b.

TABLE 45. EXPANDABLE BEAD FOAM EMISSIONS AND RELEASE POINT ESTIMATION

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Preexpansion	Reactor Vent	Volatile Monomer - vinyl chloride - styrene
		Expansion Agent - n-pentane - isopentane
		Decomposition Product - HCl (from PVC)
Cooling/Storage	Fugitives	Polymer Particulates - polyvinyl chloride - polystyrene
		Additive Particulates
Molding	Steam Holes Fugitives	Volatile Monomer - see list above.
		Expansion Agent - see list above.
		Decomposition Product - HCl
Trimming/Cutting	Fugitives	Polymer Particulates
		Additive Particulates

SECTION 9

EXTRUDED THERMOPLASTIC FOAMS

FUNCTION

Thermoplastic extrusion foams are produced by incorporating a gas-forming expanding agent into thermoplastics and extruding them under carefully controlled conditions. Depending on the type of expanding agent used, extruded foams can be in the low bulk density range 48 to 320 kg/m^3 (3 to 20 lb/ft^3) or in the medium to high bulk density range 320 to 820 kg/m^3 (20 to 50 lb/ft^3).[10]

The combination of low material costs and desirable mechanical properties for extruded thermoplastic foams have created rapid market expansion in the past few years. Packaging and building products are the major applications for extruded foam products.

INPUT MATERIALS AND END PRODUCTS

Most thermoplastics have experimentally been extruded into foam; however, the market is dominated by:

Acrylonitrile-Butadiene-Styrene (ABS)
High Density Polyethylene (HDPE)
Polypropylene
Polystyrene
Polyvinyl Chloride (PVC)

Each polymer must be formulated in order to provide the properties necessary in the final product. Additive "recipes" are designed specifically for a polymer application and are usually considered proprietary information by processors. Such formulations are similar to those used for solid polymer extrusion, and like solid extrusion, are dependent upon the processing conditions and end use requirements of the specific polymer. More information on the major plastics additives used in extruded thermoplastic foam can be found in the Extrusion and Industry Description sections of this document.

Blowing agents are unique to foam processing, and can be either physical blowing agents, such as low boiling hydrocarbons and halocarbons or chemical blowing agents which decompose upon heating to form gaseous materials.

Extruded thermoplastic foams are utilized for the production of packaging and building products. A large volume application is foam polystyrene sheet to be used for meat and produce trays, egg cartons, and snack food service.

Cups, containers, and glass bottle shields also account for a substantial volume. The largest volume of extruded foam products are actually stock products which require further fabricating to become final products. These fabrication operations include cutting, shaping, cementing, and thermoforming. Table 46 presents typical blowing agents and end products for extruded thermoplastic foams.

The extrusion of thermoplastic foams is most commonly performed with either dry blended chemical blowing agents or by direct injection of solvent blowing agents into the polymer melt. The characteristics of commonly utilized blowing agents are shown in Table 47.

In applications utilizing chemical blowing agents, the agents are dry blended with the polymer prior to extrusion processing. The blend is 0.5 to 3 percent chemical blowing agent.[149] Chemical blowing agents are dry powdered chemicals which decompose at specific temperatures into large volumes of gas. Polymers which commercially utilize chemical blowing agents include polyvinyl chloride, polystyrene, acrylonitrile-butadiene-styrene, and polypropylene.

Extrusion operations utilizing solvent blowing agents employ a liquid which will boil to produce gas at the extrusion temperature. Polyethylene and polystyrene commercially use solvent blowing agents. Nucleating agents such as talc or finely divided calcium carbonate must be included in the polymer formulation when solvent blowing agents are used in order to promote fine foam cell formation.

A typical formulation for rigid PVC foam, using a chemical blowing agent, is shown below:[67]

Material	Parts by Weight
PVC Dispersion Grade Resin	100
Acetone (increases blowing agent efficiency)	70
Dibasic Lead Phosphite (stabilizer)	10
N,N'-Dimethyl-N,N'-Dinitrosoterephthalamide (blowing agent component)	17.5
White Mineral Oil (blowing agent component)	7.5

PROCESS DESCRIPTION

Extruded thermoplastic foam products are most often produced by one of two methods. The first of these involves incorporating dry-blended chemical blowing agents with the polymer prior to extrusion. The second injects a liquid solvent blowing agent into the polymer melt prior to the extrusion die.

In dry blending operations, chemical blowing agents are blended with the polymer in the extruder feed hopper along with colorants and other additives. The blend is then extruded on conventional extrusion equipment. As the melt reaches the extrusion temperature, the chemical agent decomposes into large quantities of gas. Proper mixing screw design is important in order to assure good foam cell formation and accurate temperature control so that the foam has the proper bulk density and surface finish. Foams produced by this process

TABLE 46. EXTRUDED THERMOPLASTIC FOAM INPUT MATERIALS AND END PRODUCTS

Polymer	Blowing Agent	Product
Acrylonitrile-Butadiene-Sytrene (ABS)	p-Toluenesulfonyl semicarbazide	Piping: drain pipes waste pipes vent pipes Telephone conduit Wood-like profiles
Polycarbonate	Nitrogen	
Low Density Polyethylene (LDPE)	Fluorocarbons	Planks Rounds Thin sheets Tubes
High Density Polyethylene (HDPE)	Azodicarbonamide 4,4'-oxybis(benzenesulfonyl hydrazide) dinitrosopentamethylenetetramine p-Toluenesulfonyl semicarbazide	Flotation items Sheet for packaging
Polypropylene	p-Toluenesulfonyl semicarbazide	Decorative novelties Ribbon
Polystyrene	Pentane Halocarbons p-Toluenesulfonyl semicarbazide	Graphic art sheet Insulation board Loose fill packing of various shapes Sheet for thermoforming: produce trays egg cartons meat trays snack food service Wood-like profiles

(continued)

TABLE 46 (continued)

Polymer	Blowing Agent	Product
Polyvinyl Chloride (PVC)	4,4'-oxybis(benzenesulfonyl-hydrazide) 3,3'-Sulfonbis(benzenesulfonyl hydrazide) N-Dinitrosopentamethylenetetramine Azodicarbonamide p-Toluenesulfonyl semicarbazide Nitroso compounds	Door molding Piping: drain pipes vent pipes waste pipes Telephone conduits Trims Wood-like parts: baseboards railings

Sources: Baird, R. J., Industrial Plastics, 1971, p. 213.

Hawley, Gessner G., The Condensed Chemical Dictionary, 1977.

Nass, Leonard I. (ed). Encyclopedia of PVC, 1977, p. 814.

Nissel, F. R., "Extruding Thermoplastic Foams," Modern Plastics Encyclopedia 1981-1982, p. 296.

Suh, K. H. and R. E. Skochdopole, "Foamed Plastics," Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Edition, Vol. 11, p. 87.

TABLE 47. FOAM EXTRUSION BLOWING AGENTS

Chemical Blowing Agents	Decomposition Temperature, °C	Gases Released
Azodicarbonamide	220	N_2, CO_2, CO, NH_3
4,4'-Oxybis(benzenesulfonyl hydrazide)	150 - 190	N_2
p-Toluene sulfonyl semicarbazide	193	N_2, CO_2, CO, NH_3
5-Phenyl tetrazine	230	N_2
N-dinitrosopentamethylene-tetramine	190 - 200	
3,3'-Sulfonbis(benzene-sulfonyl hydrazide)	148	
Azobisisobutyronitrile	105	N_2

Physical Blowing Agents	Boiling Point, °C
Isopentane	27.9
Carbon Dioxide	-78.5
Nitrogen	-195.8
Ammonia	-33.4
Fluorocarbon-11 (monofluorotrichloromethane)	23.6
Fluorocarbon-12 (dichlorodifluoromethane)	-29.8
Methylene Chloride	40
Pentane	36.1

Sources: Levy, S., Plastics Extrusion Technology Handbook, 1981, p. 189.

Hawley, Gessner, Condensed Chemical Dictionary, 1977.

Nass, Leonard I., ed., Encyclopedia of PVC, 1977, p. 814.

fall in the medium to high bulk density range. Profiles extruded by this method are often sized by vacuum sizers a short distance from the die. Extrusion operations often employ water quench systems to cool the extruded profiles. A simplified block diagram of dry blend foam extrusion operations is presented in Figure 35.

Liquid solvent blown foam extrusion is the most widespread and economical method of producing low density extruded thermoplastic foams.[149] The formulated polymer is softened in the extruder barrel and the solvent blowing agent is injected into the melt under high pressure to prevent the liquid from boiling. This is carried out in a single or twin screw extruder with a screw specifically designed for plasticating and mixing. The blowing agent is injected through one or more orifices in the extruder cylinder either by a piston or diaphragm pump.

The polymer/blowing agent mixture is then cooled to a lower temperature and a high viscosity usually in a second extruder. This extruder is a larger, specially designed, cooling extruder. It is designed to maximize cooling and conveying rates while minimizing shear energy and screw speed. Cooling extruders are equipped with cooling jackets and cooling water circulation systems. The desired extrusion temperature must be carefully controlled in order to provide a uniformly cooled melt to the die. The cooled melt is then extruded through the die. The blowing agent boils just after emergence from the die due to the release in pressure.

Foam sheet is usually produced by this extrusion process through dies which produce a cylinder of thin foam sheet. Air cooling rings are sometimes used close to the die exit to cool the sheet surface. The cylindrically shaped sheet is then run over a cooled sizing mandrel and is slit to produce one or two flat sheets. The sheet is air cooled and passed through pull rolls after which it is either wound into rolls or cut into sheets. Foam sheet often continues directly to thermoforming operations. A block diagram of solvent injection foam extrusion operations is shown in Figure 36.

OPERATING PARAMETERS AND UTILITY REQUIREMENTS

Process temperatures and pressures must be carefully controlled during foam extrusion operations in order to maintain the proper polymer melt viscosity. Exact melt viscosities are crucial for the production of high quality foams with uniform cells. If the melt viscosity is too low, the foam cells will rupture as the blowing agent expands. Therefore, process temperatures need to be carefully determined for each application. Most processors use company guidelines to determine rough settings for the temperature, pressure, and screw speed. The process is then fine tuned by trial and error to determine the optimum operating parameters. Extruder cooling and heating requirements are then determined to maintain the necessary operating parameters.

Typical foam extrusion temperatures are illustrated in Table 48 for the commonly extruded polymers. The temperatures range from 175 to 230°C, and are similar to those used in solid extrusion.

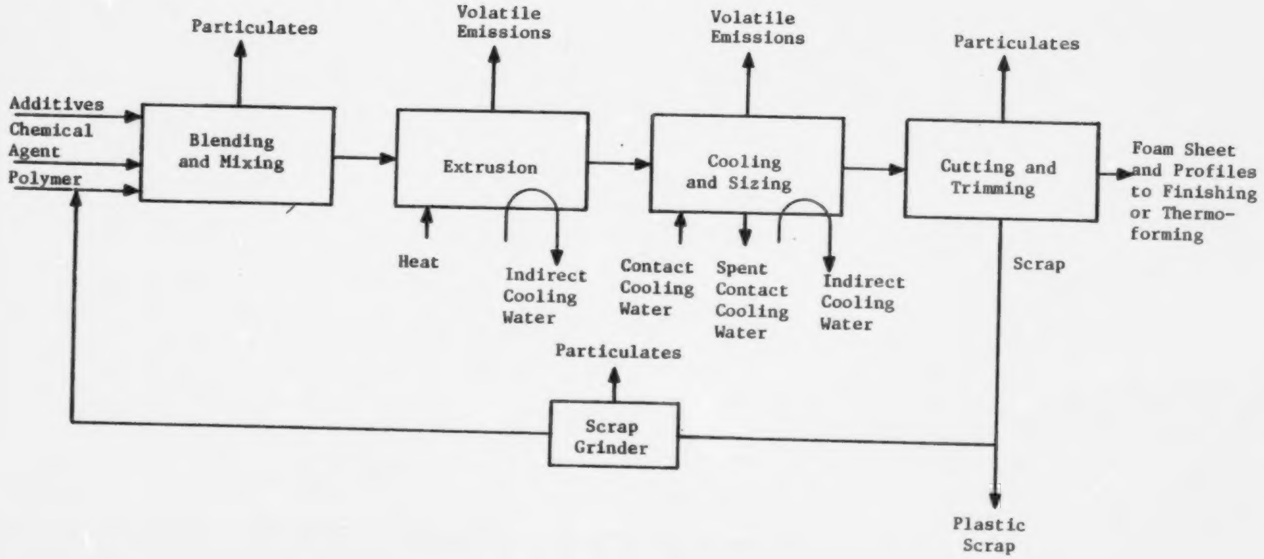
Particulates
Volatile Emissions
Volatile Emissions
Particulates
Additives
Chemical Agent
Polymer
Blending and Mixing
Extrusion
Cooling and Sizing
Cutting and Trimming
Foam Sheet and Profiles to Finishing or Thermo-forming
Heat
Indirect Cooling Water
Contact Cooling Water
Spent Contact Cooling Water
Indirect Cooling Water
Scrap
Particulates
Scrap Grinder
Plastic Scrap

Figure 35. Foam extrusion-chemical blown.

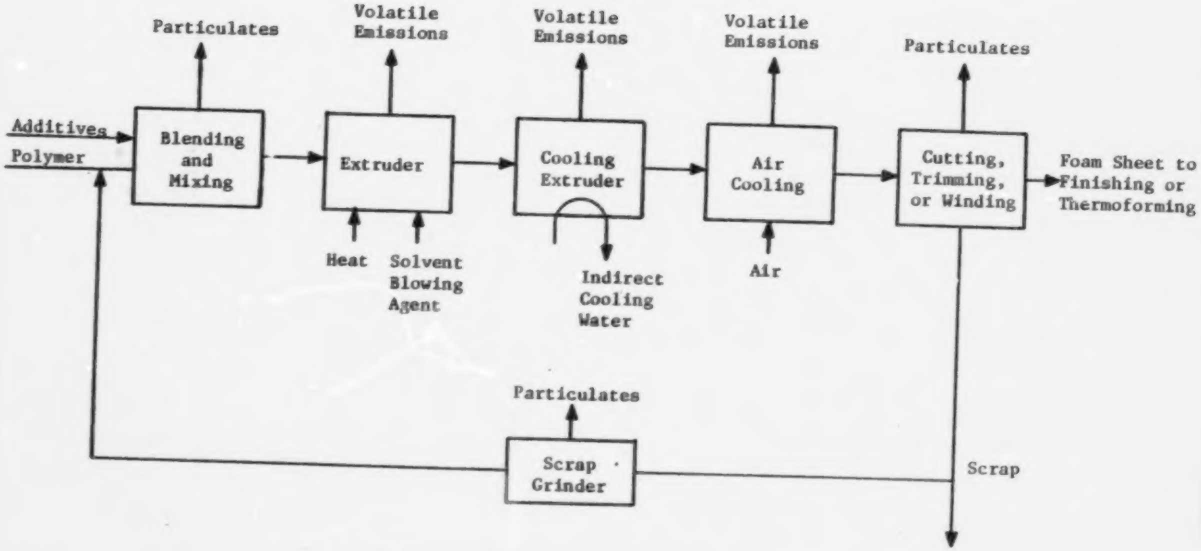
Particulates
Volatile Emissions
Volatile Emissions
Volatile Emissions
Particulates
Additives
Polymer
Blending and Mixing
Extruder
Cooling Extruder
Air Cooling
Cutting, Trimming, or Winding
Foam Sheet to Finishing or Thermoforming
Heat
Solvent Blowing Agent
Indirect Cooling Water
Air
Particulates
Scrap Grinder
Scrap

Figure 36. Foam extrusion-solvent blown.

TABLE 48. TYPICAL FOAM EXTRUSION MELT TEMPERATURES

Polymer	Melt Temperature °C
Acrylonitrile-Butadiene-Styrene (ABS)	175 - 230
High Density Polyethylene (HDPE)	200 - 230
Polypropylene	200 - 230
Polystyrene	190 - 230
Polyvinyl Chloride (PVC)	190 - 210

Source: DuBois, J. H. and F. W. John, Plastics, 1981, p. 128.

In solvent blowing agent applications, feed pressures to the cooling extruder are usually around 3.4 x 10^7 Pa (5,000 psi).[149]

WASTE STREAMS AND EMISSIONS

Thermoplastic foam extrusion operations produce air emissions, wastewater, and solid waste. Table 49 presents a summary of the point source emissions from extrusion operations. Particulates are formed by the storage, mixing, cutting, and trimming operations. Volatile emissions are released from the extruder cylinder and the exposed sheet surfaces. Wastewater is produced during product cooling. Cutting and trimming results in solid waste. Emissions and wastes are discussed in more detail in the text below. Waste streams and emissions resulting from major plastics additives used in foam are presented in more detail in the Industry Description section of this document.

Air Emissions - All foam extrusion operations have the potential to produce particulates and volatile emissions during the handling of the polymer and additives prior to and during processing. Particulates are emitted from the storage, blending and mixing of the polymer and additives prior to extrusion. When chemical blowing agents are used, they are blended prior to extrusion and may also contribute to particulate emissions. The cutting and trimming of extruded foam parts is also a source of particulate emissions. These particulates contain polymer and additive particles. Particulates are also formed during the grinding of foam scrap.

Volatiles such as traces of unreacted monomer, moisture, or decomposition products are vented from the melt at some point along the extruder cylinder axis. Decomposition products occur when excess heat causes the polymer to decompose. Table 50 presents these decomposition products which could be formed during foam extrusion along with the temperature above which it is likely to be formed.

The extrusion of foam sheet exposes large surface areas as they are cooled. There is a tendency for some polymer foams to lose, by volatilization, residual monomer and blowing agent left in the polymer. These volatiles are in such low concentration that control would be difficult and with proper ventilation should present no problems. Some blowing agent residues are incompatible with the foamed plastic. These residues can be driven off the polymers in annealing ovens or removed by water washing. The volatilization of these sometimes toxic residues (e.g., tetramethylsuccinonitrile) can pose a significant health hazard.[143]

Wastewater - Wastewater is produced during those cooling operations which utilize direct contact cooling water to cool the extruded foam parts. These direct contact cooling water streams contain dissolved volatiles and suspended polymer, chemical blowing agent residue, plasticizer, and additive particles from contact with the polymer foam.

Solid Waste - Thermoplastic foam scrap resulting from trimming operations can usually be ground and reprocessed in the extruder. The ratio of virgin thermoplastic to reground scrap must be carefully maintained in order to assure quality extrudate. A large number of foam extruders are now operated

TABLE 49. THERMOPLASTIC FOAM EXTRUSION POINT SOURCE EMISSIONS

	Air Emissions							Wastewater				Solid Waste		
	Particulates			Volatiles										
	Polymer	Additives	Chemical Blowing Agents	Monomer	Plasticizer	Decomposition Products	Excess Blowing Agent	Polymer	Plasticizer	Additives	Dissolved Volatiles	Polymer	Plasticizer	Additives
Storage, Blending, and Mixing	X	X	X											
Extruder(s)				X	X	X	X							
Cooling				X			X	X	X	X	X			
Cutting, Trimming, and Grinding	X	X	X									X	X	X

TABLE 50. DECOMPOSITION PRODUCTS

Polymer	Highest Processing Temperature (°C)†	Decomposition Temperature (°C)§	Decomposition Products
Acrylonitrile-Butadiene-Styrene (ABS)	230	300	*
Polyethylene (HDPE)	230	100	Ketone carbonyl groups form due to oxidation
Polypropylene	230	300	*
Polystyrene	230	300	*
Polyvinyl Chloride (PVC)	210	100	HCl

---

*Decomposition products are not formed at or near foam extrusion processing temperatures.

†This is the highest possible temperature reached by normal foam extrusion operations.

§This is the lowest temperature at which decomposition products begin to form.

in conjunction with thermoforming operations. In these situations, the scrap thermoplastic from thermoform operations can also be recycled to the foam extruder.

Excess scrap and particulates which cannot be recycled must be disposed of as solid waste. Since ABS, HDPE, and polypropylene waste is comprised of primarily inert plastic material, it will pose no hazardous disposal problems.

Problems may be presented by the disposal of polystyrene and polyvinyl chloride wastes. Polystyrene and styrene have reportedly caused tumors in animals during tests conducted and reported by NIOSH.[107,108] PVC formulations commonly contain di-(2-ethyl-hexyl) phthalate (DEHP). DEHP is currently suspect as a carcinogen as a result of test data which indicates that it may cause cancer in rats.[149]

WORKER DISTRIBUTION AND EXPOSURE

The number of workers employed in thermoplastic foam extrusion operations depends primarily on plant size: plants housing multiple extruding machines obviously will employ more people than single-line plants. In larger plants, operations such as scrap grinding and recycle are typically fully automated. Estimates of worker distribution, based on manhour requirements of basic extrusion equipment, are shown below:

Unit	Worker/Unit/8-hour Shift
Blending/Mixing (Batch)	1.0
Extrusion	0.5
Trimming	0.25
Scrap Grinding	0.25

Employees assigned to thermoplastic foam extrusion plants may be exposed to both particulate emissions from blending and cutting operations and gaseous emissions from the extrusion and cooling steps of the process. Potential contaminants and release points identified from the literature are summarized in Table 51. Toxicity information for these contaminants is given in Appendix C and discussed in detail in IPPEU Chapters 10 and 10b.

TABLE 51. EXTRUDED THERMOPLASTIC FOAM EMISSIONS AND RELEASE POINT ESTIMATION

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Extrusion	Extruder Barrel Vent Extruder Head Fugitives	[1]Volatile Monomer - acrylonitrile - 1,3-butadiene - styrene - bisphenol-A - propylene - ethylene - 1-butene - 1-hexene - 1-octene - vinyl acetate - vinyl chloride
		Volatile plasticizer - di-n-octyl phthalate - diisooctyl phthalate - diisodecyl phthalate - di-(2-ethylhexyl) phthalate
		Decomposition Products - ketone carbonyls (from polyethylene) - HCl (from polyvinyl chloride) - tetramethyl succinonitrile (from polystyrene)
		Solvent Blowing Agents - halocarbons - pentane - isopentane

(continued)

TABLE 51 (continued)

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Extrusion (continued)	Extruder Barrel Vent Extruder Head Fugitives (continued)	Blowing Agent By-Product - N_2 - CO_2 - CO - NH_3
Cooling	Fugitives	Residual Volatile Monomer
		Residual Decomposition Products
Storage, Mixing, Blending	Extruder Hopper Materials Handling Fugitives	[2]Polymer Particulates - ABS - polystyrene - polyolefins - polyvinyl chloride - polycarbonates
		[3]Additive Particulates
		Dry Chemical Blowing Agents - p-toluenesulfonyl semi carbazide - azodicarbonamide - 4,4'-oxybis (benzene sulfonyl hydrazide) - pentane - halocarbons - 3,3'-sulfonbis benzene-sulfonyl hydrazide

(continued)

TABLE 51 (continued)

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Storage, Mixing, Blending (continued)		- n-dinitrosopentamethylenetetramine - p-toluenesulfonyl semicarbazide - fluorocarbons - N_2
Cutting/Trimming/ Grinding	Fugitives	[2]Polymer Particulates
		[3]Additive Particulates
		Dry Chemical Blowing Agents
	Cutting and Grinding Machinery	Noise

---

[1] Principal monomers used to produce the plastics typically extruded. Other monomers or comonomers may also be present.
[2] Polymers typically extruded. Other polymers may be extruded for specialty applications.
[3] Additives will vary widely with product specifications.

SECTION 10

MULTICOMPONENT THERMOSET FOAMS

FUNCTION

Multicomponent foam processing involves pouring or injecting a chemical mixture into a mold where it reacts and expands to fill the cavity with thermosetting cellular plastic. The cellular composition of the foam is produced by blowing agents which expand the polymer. Blowing agents are either generated as a by-product of the chemical reaction or added to the input materials and are vaporized by the heat of reaction.

Polyurethane foam items comprise most of the foam product market; however, isocyanurate, phenolic, carbodiimide, and polyester are also utilized. Multicomponent foams are generally either cast in a mold or foamed in-place to produce foam products used primarily for insulation and cushioning.

INPUT MATERIALS AND END PRODUCTS

Commercially processed multicomponent thermosets include:

Carbodiimide
Isocyanurate
Phenolic
Rigid polyester
Polyurethane
Urea Formaldehyde

Acrylic, epoxy, flexible polyester, silicone, and vinyl ester foams have been prepared by multicomponent processing in developmental work using azo compounds as blowing agents.[92] To date they are not commercially processed.

Many resin suppliers offer chemical formulation systems comprised of two or three components for the commonly used thermoset foams. Such systems greatly simplify multicomponent foam production for the processor. Table 52 presents the input components, the blowing agents, and typical products for commercial multicomponent systems. More information on major plastics additives used in multicomponent thermoset foams is presented in the Industry Description section of this document.

Multicomponent thermoset foam processing can produce rigid, flexible, or elastomeric foams in a wide range of strengths and densities depending on the formulation. Major uses for thermoset foams are in insulation and cushioning applications as seen in Table 52.

TABLE 52. MULTICOMPONENT FOAM FORMULATIONS AND PRODUCTS

Foam/Typical Bulk Density	Input Components	Blowing Agent	Products
Carbodiimide 16 kg/m^3 (1 lb/ft^3)	1. polymeric isocyanate 2. catalyst	CO_2 (liberated by the reaction)	insulation foam buns
Isocyanurate 29 to 37 kg/m^3 (1.8 to 2.3 lb/ft^3)	1. isocyanate 2. catalyst 3. urethane usually incorporated for flexibility	halocarbons	insulation foam buns foamed in-place: insulation panels
Phenolic 13 to 112 kg/m^3 (0.8 to 7 lb/ft^3)	1. phenolic resol with colorants 2. acid catalyst	halocarbons or diisopropyl ether p,p-Oxybis(benzene sulfonyl hydrazide)	cores for boat hulls cores for plywood insulation foam bunstock pipe insulation
Polyester 320 to 480 kg/m^3 (20 to 30 lb/ft^3)	1. resin 2. cure initiator: t-Butyl perbenzoate 3. Additives such as: glass fiber reinforcements colorants flame retardants	t-alkylazoalkanes inorganic carbonate and acid	core material for laminates spray-on applications using glass fibers
Polyurethane 32 to 480 kg/m^3 (2 to 30 lb/ft^3)	1. isocyanate sometimes contains surfactants (for cell stabilization, blowing agent, and flame retardants) 2. resin (polyol) generally contains blowing agent, cell stabilizers, catalysts, flame retardants, and other additives such as antioxi-	flexible and in-situ foams: water blown: produce CO_2 by reaction of H_2 with isocyanate rigid foams: halocarbons such as dichlorodifluoro methane volatilized by heat of reaction other formulations: use both water and halocarbon blowing agents such as: methylene chloride	athlete equipment automobile arm and head rests, dash and crash pads and door panels boat flotation compartments cabinet doors for TVs and stereos drawer fronts duck decoys furniture frames insulation for refrigerator trucks, rail cars, and ships

(continued)

TABLE 52 (continued)

Foam/Typical Bulk Density	Input Components	Blowing Agent	Products
Polyurethane (continued)	dants, colorants, flow controllers, modifiers, plasticizers, UV stabilizers 3. Catalyst may be added separately for highly reactive formulations		life saving rings and floats packaging plaques safety equipment simulated beams small furniture parts toys carpet underlay cushioning insulation for buildings, tanks and pipelines mirror and picture frames chair shells, frames, arms, and legs
Urea Formaldehyde 16 kg/m^3 (1 lb/ft^3)	1. urea formaldehyde 2. water 3. catalyst: phosphoric acid (75%)	quaternary ammonium salts	foamed in-place insulation and panels

Sources: Agranoff, Joan (ed). Modern Plastics Encyclopedia, 1981, p. 12.

Baird, R. J., Industrial Plastics, 1971, p. 276.

Doyle, E. N., The Development and Use of Polyurethane Products, 1971, p. 232.

Frados, Joel, ed., Plastics Engineering Handbook, 1976, p. 512.

Herbert, V., "Multicomponent Liquid Foam Processing," Modern Plastics Encyclopedia 1981-1982, p. 305.

The International Plastics Selector, Inc., Foams 1978.

Grayson, Martin (ed). Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Edition, Vol. 17, p. 384.

Stott, P. E. and J. Annemiller, "A New Way to Foam Unsaturated Polyester," Modern Plastics, July 1981, p. 72.

Several examples of multicomponent thermoset foams are given below. A typical formulation for a self-skinning polyurethane foam, used to produce shoe soles, is shown below:[223]

Material	Parts by Weight
Polyether Polyol	100
Chain Extender	0-30
Curing/Cross-Linking Agent	0-8
Tertiary Amine Catalyst	0.2-2.0
Tin Catalyst	0.005-0.025
Pigment Pastes/Light Stabilizers	3-10
Fluorocarbon 11 (trichlorofluoromethane) (blowing agent)	16-30
Methylene Chloride (blowing agent)	0-7
Polyisocyanate (reactant)	Index 80-110

A typical furniture-grade polyurethane foam with a density of 1.4 to 1.5 pounds per cubic foot, has the following formulation:[74]

Material	Parts by Weight
Polyol (a polyether triol with M.W. of 3,000 and Hydroxyl No. 56)	100
TDI (80:20 isomer mixture (2,4 and 2,6))	41-50
Water	3.1-4.1
Catalysts (often stannous octoate)	0.5-1.5
Surfactant (usually silicone copolymers)	1.0-2.0
Fluorocarbon 11 (blowing agent)	2-4

A typical formulation for a rigid polyurethane foam is shown below:[74]

Material	Parts by Weight
Polyol (mixture with resultant hydroxyl number 450)	100
Flame Retardant (such as Fryol 6, Stauffer Chem. Co.)	0-15
Polymeric MDI (reactant)	110-140
Catalysts (dibutyltin dilaurate and a tertiary amine)	1.5-3
Surfactant	1.5-3
Fluorocarbon 11 (blowing agent)	25-35

A typical high density epoxy foam formulation is shown below:[67, 129]

Material	Parts by Weight
Epoxy Resins, 450 mol. wt.	100.0
Celogen (Naugatuck Chem. Co.) (blowing agent)	2.0
Tween 20 (Atlas Chem. Co.) (emulsifier)	0.1
Toluene (reduce viscosity)	5.0
Diethylenetriamine (curing agent)	6.0

PROCESS DESCRIPTION

Multicomponent thermoset foam processing is a complex process since it is based upon the chemical reaction of two input streams. The success of the process is highly dependent upon the temperature of the input components, the humidity of the ambient air, the input ratio of the components, and the mold design parameters. A block diagram of multicomponent foam processing is shown in Figure 37.

Prior to mixing, the liquid feeds are stored in pressurized storage tanks.[92] The storage tanks are usually jacketed and agitated to control temperatures and maintain the homogeneity of the liquid. The liquid components are metered through heat exchangers to the mixing head. Most mixing heads have three-way valves which allow recirculation of the components to the storage tanks between use. The input components are thoroughly mixed at the mixing head and are subsequently poured into a mold or injected for foam in-place applications.

Molds for this process are generally machined or cast two-part aluminum molds which can be separated after the part has cured to allow removal. Foam in-place applications are similar except that the mold is the actual product such as a resin being foamed inside the cavities of refrigerator door shells. Portable dispensing units are often used to permit fast filling and on-site insulation applications.

Another application of foam in-place technology is used for the production of polyurethane foam slabs. The polyurethane components are mixed and are discharged onto a surface such as a moving paper web. The production of CO_2 gas by the reaction causes the foam to form a continuous slab. The slab is then exposed to radiant heat in an oven which completes the cure. The slab is then cut into blocks according to the production requirements.

Foam is formed through the generation of gaseous cure reaction by-products or by the addition of an auxiliary blowing agent. The cure reaction by-products can form foams by two methods. First, the reaction of two of the input components in thermoset foams may release a gaseous by-product which expands the thermoset to produce a foam. For example, polyurethanes release CO_2 upon polymerization of the isocyanate and the polyol. In the second mode, the additives used in the thermoset polymerization, for example, free radical initiators, both polymerize the resin and decompose to form gaseous by-products. This process is used for producing unsaturated polyester foams with azo compounds.

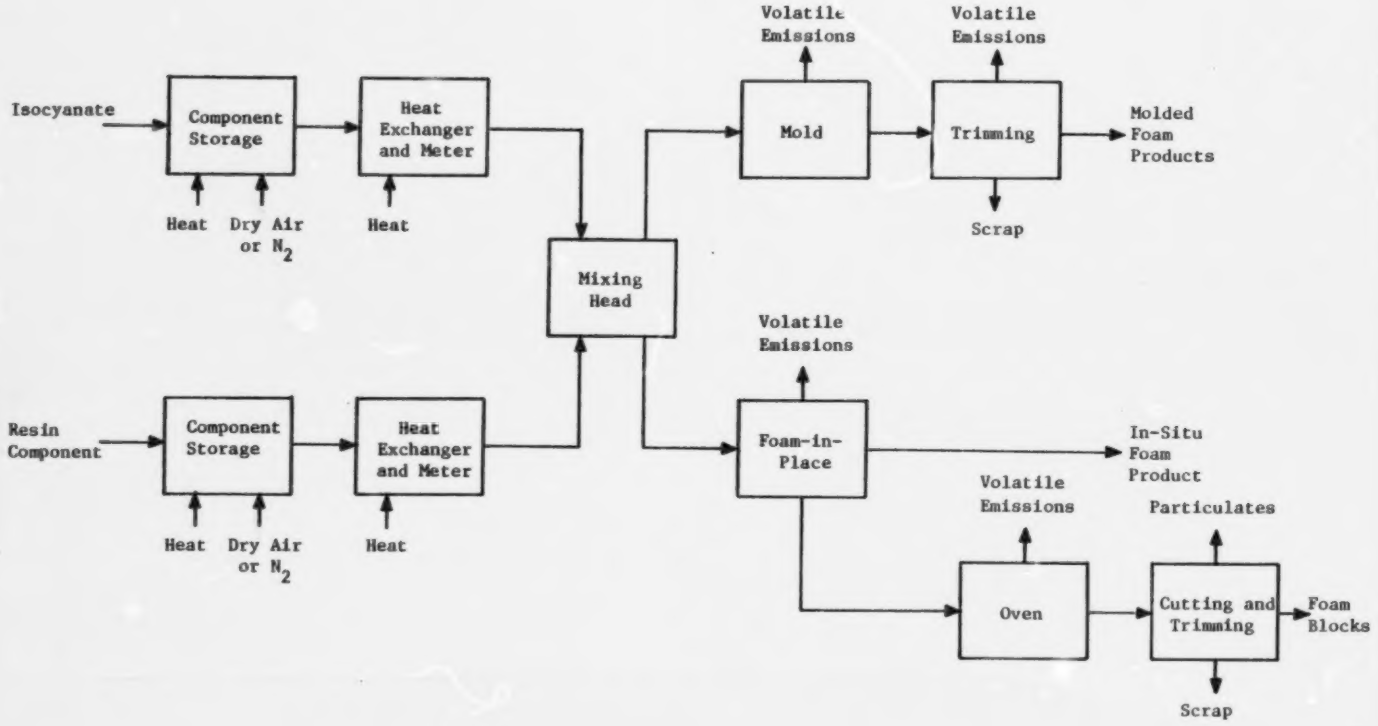
Isocyanate
Component Storage
Heat
Dry Air or N2
Heat Exchanger and Meter
Heat
Resin Component
Component Storage
Heat
Dry Air or N2
Heat Exchanger and Meter
Heat
Mixing Head
Volatile Emissions
Mold
Volatile Emissions
Trimming
Molded Foam Products
Scrap
Volatile Emissions
Foam-in-Place
In-Situ Foam Product
Volatile Emissions
Oven
Particulates
Cutting and Trimming
Foam Blocks
Scrap

Figure 37. Multicomponent thermoset foam processing.

Auxiliary blowing agents also have two forms. First, gas blowing agents such as nitrogen are introduced directly into the polymer melt prior to its injection into the die or mold. This method is commonly used for processing thermoplastic foams. The second mode involves combining blowing agents in the input stream. The processing temperature or the heat or cure reaction causes the agent to vaporize thereby forming a foam.

Since the reaction components are metered together in exact amounts for each application, very little thermoset scrap is formed in mold applications and none is formed during foam in-place applications. In situations where mold overflow or part or slab trimming or cutting does produce scrap, it cannot be recycled and must be disposed of as scrap.

OPERATING PARAMETERS AND UTILITY REQUIREMENTS

The temperatures utilized during multicomponent thermoset foam processing are crucial to the successful production of foam parts. Chemical components must be maintained at proper temperatures to insure accurate pumping, flow rates, mixing characteristics, and chemical reactivity.[92] Typical component metering temperature are shown below:

Foam Type	Temperature °C
Carbodiimide	21 - 38
Isocyanurate	21 - 38
Phenolic	27 - 32
Polyurethane	21 - 38

Source: Herbert, V., "Multicomponent Liquid Foam Processing," Modern Plastics Encyclopedia 1981-1982, p. 305.

Mold pressures generally range from 3.4×10^4 to 20.6×10^4 Pa (5 to 30 psi) depending on the system type and mold design.[92]

WASTE STREAMS AND EMISSIONS

Multicomponent foam operations produce air emissions and solid waste. Wastewater is not produced since cooling water is not used during multicomponent foam processing. Table 53 presents a summary of the point source emissions from multicomponent foam operations. Emissions and wastes are discussed in more detail in the text below. Major plastics additives in this foam process which produce waste streams and emissions are discussed in more detail in the Industry Description section of this document.

Air Emissions - Multicomponent foam operations have the potential to produce particulate and gaseous emissions. Particulates are produced by the cutting and trimming of foam parts. These particulates consist of fine particles of resin, additives, and catalyst.

Volatile emissions are released during the cure reactions which occur in the mold, oven, and in-situ during foam in-place operations. Such emissions

TABLE 53. MULTICOMPONENT THERMOSET FOAM POINT SOURCE EMISSIONS

	Air Emissions						Solid Waste		
	Particulates			Volatiles					
	Resin	Additives	Catalyst	Isocyanates	Cure Reaction By-Products	Excess Blowing Agents	Resin	Additives	Catalyst
Loading				X					
Mold				X	X	X			
Foam-In-Place					X	X			
Oven Heating					X	X			
Cutting and Trimming	X	X	X				X	X	X

consist of cure reaction by-products and vaporized carbon dioxide and halocarbon blowing agents. Decomposition products are not formed during multicomponent foam production due to the low processing temperatures. Fugitive emissions of uncured isocyanates may be released in this process. They can cause skin, eye, and respiratory tract irritation.

Solid Waste - Very little thermoset foam scrap is generated by multicomponent foam processes since the reaction components are metered together for each application. Scrap is produced by the trimming and cutting of foam parts. This scrap must be disposed of as solid waste. Occasionally such scrap is sold to other processors who grind it and use it as filler in lower quality product castings. Since the thermoset foam waste is comprised of inert material, it will pose no hazardous disposal problems.

WORKER DISTRIBUTION AND EXPOSURE

Worker distribution in multicomponent thermoset foam production facilities is similar to that in other foam-producing operations. We have estimated worker distribution by correlating major equipment manhour requirements with the process diagram shown in Figure 37. Estimates are shown below:

Unit	Workers/Unit/8-hour Shift
Storage	0.5
Heat Exchanger	0.125
Molding	0.5
Curing	0.5
Trimming	0.25

The principal industrial health concern in multicomponent thermoset foam production is the potential for employee exposure to unreacted isocyanates, particularly toluene-2,4-diisocyanate (TDI). Isocyanate compounds are highly irritating to the skin and mucous membranes and TDI sensitizes susceptible persons to extreme asthmatic reactions in subsequent exposures. Other contaminants to which employees may be exposed include polymer, additive, and catalyst particulates, residual blowing agents, and inert gases produced as cure by-products.

Estimated contaminants and release points are summarized in Table 54. Additional toxicity information is provided in Appendix C of this document and in IPPEU Chapters 10 and 10b.

TABLE 54. MULTICOMPONENT THERMOSET FOAM EMISSIONS AND RELEASE POINT ESTIMATION

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Storage and Loading	Fugitives	Isocyanates - TDI - MDI - PAPI - HDI
Molding	Mold Vents Fugitives	Isocyanates
		Cure By-Products - N_2 - CO_2 - CO - NH_3
		Excess Blowing Agent - halocarbons
Foam In-Place	Fugitives	Cure By-Products
		Excess Blowing Agent
Curing	Fugitives	Cure By-Products
		Excess Blowing Agent

(continued)

TABLE 54 (continued)

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Cutting/Trimming	Fugitives	[1]Polymer Particulates - polyurethane - phenolic resins - amino resins [2]Additive Particulates: Antioxidants - BHT - dilauryl thiodipropionate Colorants - carbon black - titanium dioxide - Cd sulfoselenide - phthalocyanines Flame Retardants - antimony oxide - alumina trihydrate UV Stabilizers - 2-hydroxy-4-octoxybenzophenone Urethane Catalysts - triethylene diamine - stannous octoate Reinforcers - glass fibers - silica

[1] Majority of polymer foamed is polyurethane.

[2] Specific additives listed are those documented in the literature. Many other additives may be used, depending on product specifications.

SECTION 11

STRUCTURAL FOAMS

FUNCTION

Structural foam processing produces heavy wall parts which are strong enough to be used for structural applications. Such parts are characterized by a solid surface layer with few bubbles and a core of uniformly sized bubbles. The skin layer is typically 0.08 to 0.20 cm (0.03 to 0.08 in) thick.[29]

The structural foam molding process is similar to the injection molding of solid plastic products. The difference lies in that a blowing agent is added to either the polymer input materials or the polymer melt.

Structural foam parts provide a number of advantages over solid injection molded parts. Parts which must normally be formed by assembling numerous metal and plastic parts can often be formed in one piece from structural foam. Structural foam parts show a considerable savings in raw material costs and do not contain the molded-in stresses developed due to the high pressures utilized during injection molding.[60]

INPUT MATERIALS AND END PRODUCTS

Structural foam processing is performed with thermoplastic polymers. While polystyrene is the major material used in structural foam molding, extensive research is being performed to develop structural foam products from a wide range of other thermoplastics. A complete list of polymers commercially utilized is shown below:

Acrylonitrile-Butadiene-Styrene (ABS)
Phenylene Oxide
Polycarbonate
High Density Polyethylene (HDPE)
Polypropylene
Polystyrene

Each polymer must be formulated in order to provide the properties necessary in the final foam product. Colorants, fire retardants, and UV stabilizers are frequently used to enhance the polymer qualities. Fillers are often used to reinforce the basic polymer and to lower the total material costs. Fillers are also desirable in the resin to act as nucleation points for cell development. Surfactants are important additives to foam formulations. They serve to lubricate the mold as well as control cell size and cell wall stability.[36] These additives are most often blended into the polymer melt just prior to processing. More detailed information on major plastics additives used in structural foam is presented in the Industry Description section of this document.

Blowing agents utilized for structural foam molding are similar to those utilized in extruded thermoplastic foams and can be either chemical agents or directly injected gases. Solid chemical agents which decompose at the process temperature to give gaseous products are most commonly used. The gases formed from their decomposition are inert, odorless, and non-toxic and are usually nitrogen and carbon dioxide. Commonly used chemical blowing agents include azodicarbonamide and sodium bicarbonate. They are mixed into the formulated resin in the feed hopper. Nitrogen gas is also used as a blowing agent. Gas under pressure is introduced directly into the thermoplastic resin melt as it is fed to the mold.

The applications of structural foam lies primarily in the furniture, business machine, and construction areas. Table 55 presents typical structural foam additives, blowing agents, and products.

A typical formulation for processing structural foam was not found in the literature.

PROCESS DESCRIPTION

Structural foam molding can be divided into two general processes, the low pressure process, and the high pressure process. The basis of the structural foam process is that the blowing agent gas expands causing the melt to foam and fill the mold. On contact with the cool mold surface, the gas bubbles collapse and a solid skin is formed on the foam product. A generalized block diagram of the structural foam process is shown in Figure 38.

Low Pressure Process - The low pressure process can be used to produce both large and small parts with thin to heavy walls.[3] It is particularly useful when parts with a textured finish are needed or when large and heavy parts are to be produced. The two most commonly used low pressure processes are the Union Carbide process and the Beloit process.

In the Union Carbide process, the input polymer and additives are transported from a hopper to the extruder barrel where they are mixed and plasticized by heat and the extruder screw.

The Union Carbide process generally utilizes pressurized nitrogen gas as the blowing agent. The blowing agent is introduced into the thermoplastic melt in the extruder barrel. The extruder screw feeds the melt to an accumulator where the melt is maintained at the proper temperature and at a pressure high enough to prevent expansion of the blowing agent. The accumulated melt is dispensed into the mold cavity where the entrained gas expands. As the foam hits the cold mold surface, the bubbles collapse forming a skin around the inner foam. As the newly formed part cools, the accumulator is being refilled. When the part has sufficiently cooled, it is removed from the mold by ejector pins, air blasts, or manually. The skin thickness of low

TABLE 55. STRUCTURAL FOAM

Polymer	Additives	Blowing Agents	Products
Acrylonitrile-Butadiene-Styrene (ABS)	Colorants Flame Retardants Reinforcers	Nitrogen Azodicarbonamide	Business machines Home entertainment system cabinetry Appliances Industrial machine housings Building and construction items Lab cabinetry Counter/room dividers Upholstered furniture shells Burial parts
Polycarbonate	Polymer must be dried before processing Colorants Flame Retardants		Automobile parts such as jeep tops and corvette moon roofs Electrical and communications housings for outdoor use such as repeater housing power chassis Mass transit applications such as door sills and cantilevered supports
Polyphenylene Oxide	Flame Retardants	Freon 22 Nitrogen Chemical Blowing Agent	External and internal functions of printers, typewriters, computer housings, display stations, calculators, point-of-sale terminals, copiers, and work stations Photographic film processing tanks and housings Industrial control housings Telecommunications backpanels
Polyethylene High Density (HDPE)	Fillers	Freon 22 P,p-Oxybis(benzene sulfonyl hydrazide) Azodicarbonamide	Forklift pallets Shipping crates Ducts Machine housings Portable loud speakers Railroad crossing systems

(continued)

TABLE 55 (continued)

Polymer	Additives	Blowing Agents	Products
Polypropylene	Fillers	Nitrogen Chemical Blowing Agents Nitrogen	Picture frames Decorative moldings Shipping crates Furniture Automotive components such as glove box doors, RV doors, trim and agricultural equipment Molding and carpet tacking strips
Polystyrene	Antioxidants Flame Retardants UV Stabiliziers	Azodicarbonamide Volatile liquids Methylene chloride	Egg cartons Trays Packaging Business machine and industrial housings such as computers Chair frames Shutters Natural wood look parts Building and construction uses Utility conduits Enclosures Horticultural applications

Sources: Agranoff, Joan, Modern Plastics Encyclopedia, 1981-1982, pp. 4, 30, 46.

Bakker, Marilyn, Structural Foam Molding Status 1979, 1979, pp. 21-23.

Crull, A. W., Polyurethane and Other Foams, 1979, pp. 158-171.

"Freon Blown Structural Foam is Superior," Modern Plastics, July 1981, p. 28.

The International Plastics Selector, Inc., Foams, 1978, pp. 430-435.

"Prize Winning Structural Foam Applications," Modern Plastics, July 1979, p. 52.

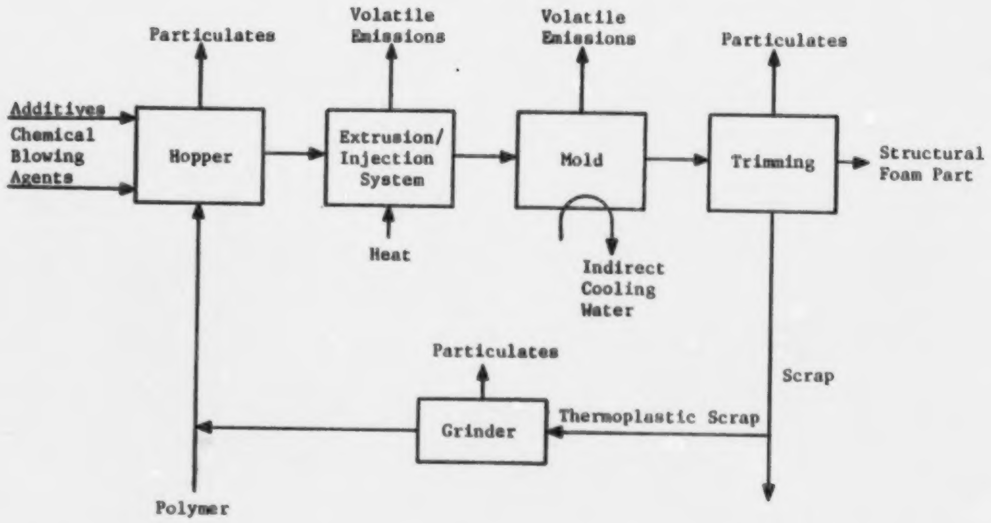
Particulates
Volatile Emissions
Volatile Emissions
Particulates
Additives
Chemical Blowing Agents
Hopper
Extrusion/ Injection System
Mold
Trimming
Structural Foam Part
Heat
Indirect Cooling Water
Particulates
Scrap
Thermoplastic Scrap
Grinder
Polymer

Figure 38. Structural foam process.

pressure molded parts depends highly upon the pressure and temperature of the melt; the type and amount of blowing agent; and the amount of melt.

The Beloit process is very similar to the Union Carbide process except that a chemical blowing agent is blended into the thermoplastic resin before extrusion. The pressure of injection from the accumulator to the mold cavity is slightly higher than that required in the Union Carbide process.[36]

High Pressure Process - The high pressure process produces foam parts with improved surface finishes over those produced by the low pressure processes. The high pressure process uses conventional injection pressure to fill the mold with polymer using a rapid injection velocity. The melt in contact with the cool mold forms a solid skin and the melt is packed so full that it cannot expand and form foam cells. After a specified period of time the mold cavity is expanded to the finished part dimensions. The blowing agent volitalizes in the inside of the part and forms a cellular core. The high pressure process is limited to parts with geometries which lend themselves to mold expansion.[36]

Finishing Operations - Structural foam parts produced by either the low pressure or high pressure process must be trimmed to remove flash and runners. Foam parts produced by low pressure processes have surfaces which are generally characterized by a swirl pattern. Low pressure process parts require finishing operations such as painting in order to have desirable product surfaces.

OPERATING PARAMETERS AND UTILITY REQUIREMENTS

The conditions under which structural foam operations are performed are strongly governed by the polymer being processed and the end product application. Most processors use company guidelines to determine rough settings for the temperature, pressure, and screw speed. The process is then fine-tuned to determine the optimum processing temperature, mold temperature, and pressure. Cooling and heating requirements are then determined to maintain the necessary operating parameters.

The injection molding of thermoplastics requires that the polymer be sufficiently plasticated in order to allow it to flow into the mold cavity. Table 56 presents typical processing temperatures for structural foam thermoplastics. The mold is cooled by indirect cooling water in order to speed part cooling.

Structural foam cycle times vary according to the design of the product and the polymer formulation being utilized. Typical cycle times are longer than for injection molding due to the insulating qualities of the foam.[60] Injection time does not exceed two seconds in order to be able to carefully control the cell size and foam density.[59] Injection pressures are on the order of 6.9×10^5 to 34.5×10^5 Pa (100 to 500 psi) during the low pressure processes. The high pressure process uses injection pressures of 3.4×10^7 Pa (5,000 psi).[59]

TABLE 56. STRUCTURAL FOAM MELT TEMPERATURES

Polymer	Temperature °C
ABS	180 - 240
Phenylene Oxide	a
Polycarbonate	280 - 310
HDPE	200 - 300
Polypropylene	200 - 275
Polystyrene	180 - 260

---

[a] Temperature not found in the reference literature.

Sources: Bown, John, Injection Molding of Plastic Components, 1979, p. 77.

Dym, J. B., Injection Molds and Molding, 1979, pp. 297-321.

WASTE STREAMS AND EMISSIONS

Structural foam operations produce air emissions and solid waste. No wastewater is produced since water is used only in the indirect cooling of the mold halves. Table 57 presents a summary of the point source emissions from structural foam operations. More information on wastes generated from major plastics additives used in structural foams is presented in the Industry Description section of this document.

Air Emissions - Structural foam operations have the potential to produce particulate and hydrocarbon emissions. Particulates are produced from the polymer feed and mixing operations in the hopper. Particulates are also produced by the trimming of the parts and the grinding of thermoplastic scrap. These particulates consist of particles of polymer, filler, and other additives. When chemical blowing agents are used they are also blended prior to extrusion and may also contribute to particulate emissions.

Volatile emissions are liberated from vents in the extrusion/injection cylinders and the molds. These emissions consist of traces of monomers, excess blowing agent gas, blowing agent residues, and decomposition products. Decomposition products occur when the processing temperature reaches that temperature at which the polymer begins to decompose. Table 58 presents those decomposition products which could be formed during structural foam operations.

Solid Waste - Thermoplastic scrap generated by the trimming of product flash can usually be ground and recycled to the hopper feed. Excess scrap and particulates which cannot be recycled must be disposed of as solid waste. The majority of this waste is comprised of inert plastic material and it will pose no disposal problems.

Problems may be presented by the disposal of polystyrene wastes. Polystyrene and styrene have reportedly caused tumors in test animals during tests conducted and reported to NIOSH.[107, 108]

WORKER DISTRIBUTION AND EXPOSURE

Structural foam production worker distribution estimates have been derived by correlating major equipment manhour requirements with the process flow diagram shown in Figure 38. We have assumed manual mold removal in the estimates below:

Unit	Workers/Unit/8-hour Shift
Mixing	0.5
Extrusion	0.5
Molding	0.5
Trimming	0.25
Scrap Grinding	0.25

Employees in structural foam manufacturing operations may be exposed to both particulate and gaseous emissions. Table 59 identifies estimated

TABLE 57. STRUCTURAL FOAM POINT SOURCE EMISSIONS

	Air Emissions							Solid Waste		
	Particulates				Volatiles					
	Polymer	Chemical Blowing Agent	Additives	Fillers	Monomer	Excess Blowing Agent	Decomposition Products	Polymer	Fillers	Additives
Hopper	X	X	X	X				X	X	X
Extrusion/Injection System					X	X	X			
Mold					X	X	X			
Trimmer	X		X	X				X	X	X
Grinder	X		X	X				X	X	X

TABLE 58. DECOMPOSITION PRODUCTS

Polymer	Highest Processing Temperature (°C)†	Decomposition Temperature (°C)§	Decomposition Products
ABS	240	300	*
Phenylene Oxide	#	#	*
Polycarbonate	310	330	*
HDPE	300	100	Ketone carbonyl groups form due to oxidation
Polypropylene	275	300	*
Polystyrene	260	300	*

---

*Decomposition products are not formed at or near structural foam processing temperatures.

†This is the highest possible temperature reached by normal structural foam operations.

§This is the lowest temperature at which decomposition products begin to form.

#Temperatures not found in the reference literature.

TABLE 59. STRUCTURAL FOAM EMISSIONS AND RELEASE POINT ESTIMATION

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Mixing/Blending	Hopper Fugitives	[1]Polymer Particulates - ABS - polycarbonates - polyphenylene oxide - polyolefins - polystyrene
		Blowing Agent Particulates - azodicarbonamide - p,p-oxybis (benzene sulfonyl hydroxide)
		[2]Additive Particulates
Extrusion/Injection	Extruder Barrel Vent Fugitives	[3]Volatile Monomer - 1,3-butadiene - acrylonitrile - styrene - 2,6-xylenol - bisphenol-A - ethylene - propylene
		Blowing Agent - methylene chloride - chlorofluorocarbons
		Blowing Agent By-Product - N_2
		Decomposition Product - ketone carbonyls (polyethylene)

(continued)

TABLE 59 (continued)

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Molding	Mold Vents Fugitives	Volatile Monomer
		Blowing Agent
		Blowing Agent By-Products
		Decomposition Products
Trimming/Scrap Grinding	Fugitives	Polymer Particulates
		Additive Particulates
		Residual Blowing Agent
	Grinder Materials Handling	Noise

---

[1] Polymers typically used for structural foam. Other polymers may be used for specialty applications.

[2] Specific additives depend on product formulation.

[3] Primary monomers used to produce the plastics typically foamed. Other monomers or comonomers may also be present.

emissions and probable release points. Toxicity information for the contaminants listed is summarized in Appendix C and discussed in detail in IPPEU Chapters 10 and 10b.

SECTION 12

LAMINATING

FUNCTION

Laminating is used to produce strong parts formed from layers of fillers and thermoset resins bonded together as a unit body. The resin and sheet layers are joined together by heat and pressure to form sheets, tubes, rods, or molded shapes. The most common use of laminating is to produce structural and decorative panels for residential and industrial uses. Laminates generally have good electrical insulating properties and are widely used in that industry.[59]

Laminated plastics are often considered a form of reinforced plastics (see Section 19). The difference lies in that most reinforced plastics require little or no pressure application whereas laminates require high pressures to complete their formation. The laminating operations fall into three general areas which will be discussed later in this section. The three areas are:

- Flat Laminate Sheets
- Laminate Rods and Tubes
- Continuous Laminating

INPUT MATERIALS AND END PRODUCTS

Laminate products are produced from thermosetting resins and filler sheets. The combination of these two inputs is determined to best suit the product requirements and specifications while keeping total product costs to a minimum.

Thermosetting resins are the major resin types used commercially since they make a harder, more solvent resistant and rigid laminate. Typical resins used for laminating are:

- alkyd polyesters,
- epoxy resins,
- melamine formaldehyde, and
- phenolic resins,

Most laminated products are flat sheets which are prepared for specific purposes such as counter tops, furniture, and wall panels. The electrical industry uses laminate products as housings for equipment when strength and electrical insulating properties are required. Table 60 presents a summary of the product types produced by each laminating process.

TABLE 60. MAJOR INPUT MATERIALS AND END PRODUCTS OF LAMINATING OPERATIONS

Process	Polymer Inputs	Typical Products
Flat Laminate Sheets	Epoxy resins Melamine formaldehyde Phenolic resins Alkyd polyesters Paper or cloth sheets	Counter tops Furniture panels Fuse boxes Terminal blocks Transformer insulation Wall and ceiling panels Cut out products such as cams and gears Printed circuit panels
Laminate Rods and Tubes	Epoxy resins Melamine formaldehyde Phenolic resins Alkyd polyester Paper or cloth sheets	Rods, tubes and other profile shapes Tanks Pressure bottles Pipe for oil fields, chemical processors, water distribution, and sewage disposal
Continuous Laminating	Alkyd polyester Chopped glass fibers	Awnings Fences Greenhouse panels Kitchen counter tops Panels Patio covers Table tops Truck and trailer panels and liners

Laminates are formed using layers of paper, cloth, glass fiber, or glass cloth as the reinforcing agents. Paper is the least expensive reinforcer. Rag paper makes the best paper filler for lamination because of its toughness; however, due to the high cost of rag papers, cheaper paper made from purified wood cellulose pulp is frequently used. Papers which are used must be absorbant by nature. Cloth fillers are made in a variety of weights ranging from thin cotton to thick canvas. Sheets of asbestos paper or fabric are used when temperature resistance is required in the final product. Glass fabric woven from very fine filaments is used to form a laminate which has a high resistance to impact, moisture and heat. For decorative purposes, colored or printed papers are used as the surface sheet. In this way laminates with the appearance of wood and marble can be produced.[59]

Phenolics are generally low in cost and have excellent electrical and physical properties. The melamines are more costly but offer flame resistance and have excellent electrical properties. The alkyd polyesters are low in cost and are used where heat resistance and electrical properties are not of prime importance. Epoxies are high in chemical resistance and are extremely moisture resistant. Table 61 presents a summary of the properties and typical additives used in thermosetting resins for laminating operations. More detailed information on major plastics additives is presented in the Industry Description section of this document.

Two typical laminating formulations are given below:[79, 95]

Material	Parts by Weight
Polyester Resin (Koppers 6060-5)	100
Methyl Ethyl Ketone Peroxide (catalyst)	0.4-0.5
Glass (reinforcing agent)	30-40

Material	Parts by Weight
Polyester Resin (Beetle L2615 BIP Chemical Ltd.)	100
Methyl Ethyl Ketone Peroxide (catalyst)	1
Cobalt Naphthenate (accelerator)	0.5
Glass (reinforcing agent)	34-57

PROCESS DESCRIPTION

The laminating process combines filler sheets and thermosetting resins by applying heat and pressure to produce strong hard products. Laminating is discussed in this section as three general processes:

- Flat Laminate Sheets
- Laminate Rods and Tubes
- Continuous Lamination.

Flat Laminate Sheets - Flat laminate sheet is produced by impregnating the base sheets with liquid thermosetting resin. Phenolics, melamines, alkyd polyester, and epoxies are all used. These resins are generally applied in a varnish form or water-based solution. The solvent may be evaporated from the

TABLE 61. ADDITIVES AND PROPERTIES FOR LAMINATING RESINS

Property	Phenolics	Melamine	Alkyd Polyester	Epoxy
Heat Resistance	Excellent	Excellent	Good	Fair
Physical Properties	Good	Good	Good	Good
Electrical Properties	Excellent	Excellent	Good	Excellent
Water Resistance	Good	Fair	Good	Excellent
Machining Properties	Fair	Fair	Fair	Good
Advantages	Good all around properties	Good all around properties	Requires only low pressure for molding	No Shrinkage
Typical Additives	Catalysts Coupling Agents Crosslinking Agent Inhibitors Neutralizers Plasticizers Promoters	Colorants Curing Agents Fillers Lubricant Plasticizers Solvents Stabilizers	Accelerators Catalysts Colorants Coupling Agents Drying Oils Fillers Flame Retardants Impact Modifiers Mold Release Agents Plasticizers Solvents Stabilizers Thixotropes UV Absorbers Viscosity Modifiers	Accelerators Catalysts Coupling Agents Flame Retardants Hardeners Impact Modifiers Mold Release Agents Reinforcers Stabilizers UV Absorbers Viscosity Modifiers

Sources: Beck, R. D., Plastic Product Design, 1980, p. 334.

McGarry, Frederick J., "Laminated and Reinforced Plastics," Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Edition, Vol. 13, pp. 972-973.

Updegraff, Ivor H., et. al., "Amino Resins and Plastics," Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Edition, Vol. 2, pp. 450-1.

filler preceding lamination. Figure 39 presents a block diagram for the formation of flat laminate sheets. The correct number of sheets for the specific application are placed one on top of each other with the resin between two platens of a hydraulic laminating press. Printed or patterned cloth or paper sheets may be included to give the laminate the desired finished appearance. Most commonly a multi-platen hydraulic laminating press is used so that more than one laminate sheet can be produced at a time. The hydraulic press closes, and pressure and heat are applied to the layers. The thermoset resin flows through the filler sheets and cures due to heat flux. The chrome plated steel platens are heated either by passing steam through channels in the platen or by electricity. After the sheets have sufficiently cured, the platens are allowed to cool, the press is opened, and the sheets removed. Allowing the platens to cool before removing the laminate helps prevent warpage. The edges of the sheets are trimmed and they then proceed to finishing operations appropriate for the final use designation. Irregular shape items such as bearings, gears, and cams are often formed by cutting the shapes from the flat laminate sheets. The shapes are then compression molded to make them stronger.[10]

Laminate Rods and Tubes - Laminate rods and tubes are produced from filler webs impregnated with thermoset resin. Phenolics, melamines, alkyd polyesters, and epoxies are all used. Figure 40 presents a block diagram of the formation of laminate rods and tubes. Solid rods are made by winding the impregnated filler web around a very thin rod (mandrel) which is then withdrawn. The preform rods are then placed in a compression mold where heat and pressure are applied (see Compression Molding - Section 14). In some operations the rods are placed in an oven and allowed to cure without pressure over a long period of time, typically 12 to 24 hours. The solid laminate rod requires the flash to be trimmed prior to further finishing. In making a tube, the mandrel is left in during the compression molding step.

Continuous Lamination - Continuous lamination is used to produce large volumes of structural grade sheets for use as residential and industrial panels. The process consists of combining resins with various reinforcements on an in-line conveyor. Polyester resins are most common in the continuous lamination process along with glass fibers which are usually used in the chopped form. Figure 41 presents a block diagram of continuous lamination.

Continuous laminated sheets are formed between two moving carrier films. The first film which creates the panel's surface is generally polyester, cellophane, or nylon and can have a smooth, embossed, or matte finish.[218] Polyvinyl fluoride films are occasionally used as the carrier film and are often left as part of the laminate product. The resin mix is metered onto the moving carrier film. The glass fibers fall onto the resin coated film and become "wetted." A second carrier film is placed on top of the mix and the resulting "sandwich" is pulled through a set of squeeze rolls to eliminate entrapped air. The laminate then enters a gas or electrically heated oven. When fully cured, the laminate leaves the oven and the carrier film is stripped from the newly formed laminate. The continuous sheet is trimmed and cut before proceeding to finishing operations.

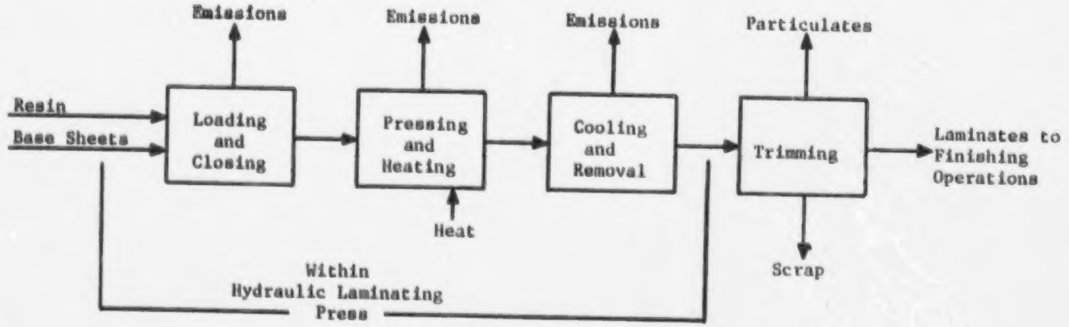
Emissions
Emissions
Emissions
Particulates
Resin
Base Sheets
Loading and Closing
Pressing and Heating
Cooling and Removal
Trimming
Laminates to Finishing Operations
Heat
Scrap
Within Hydraulic Laminating Press

Figure 39. Flat laminate sheets.

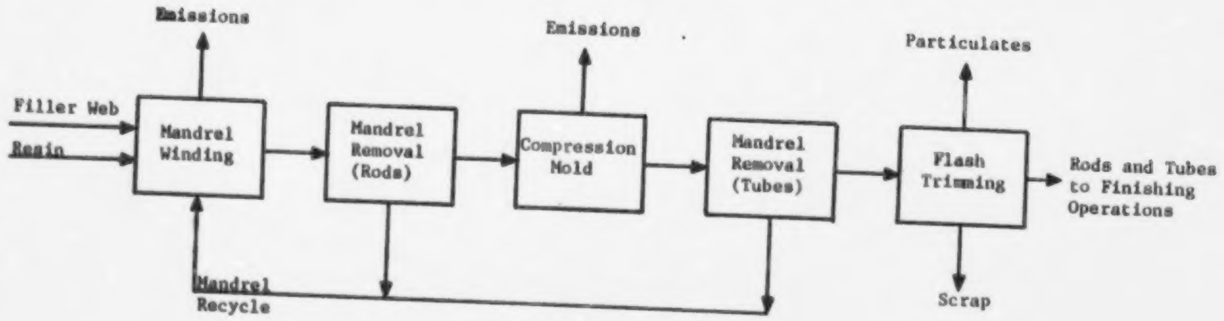
Emissions
Filler Web
Resin
Mandrel Winding
Mandrel Removal (Rods)
Emissions
Compression Mold
Mandrel Removal (Tubes)
Particulates
Flash Trimming
Rods and Tubes to Finishing Operations
Scrap
Mandrel Recycle

Figure 40. Laminate rods and tubes.

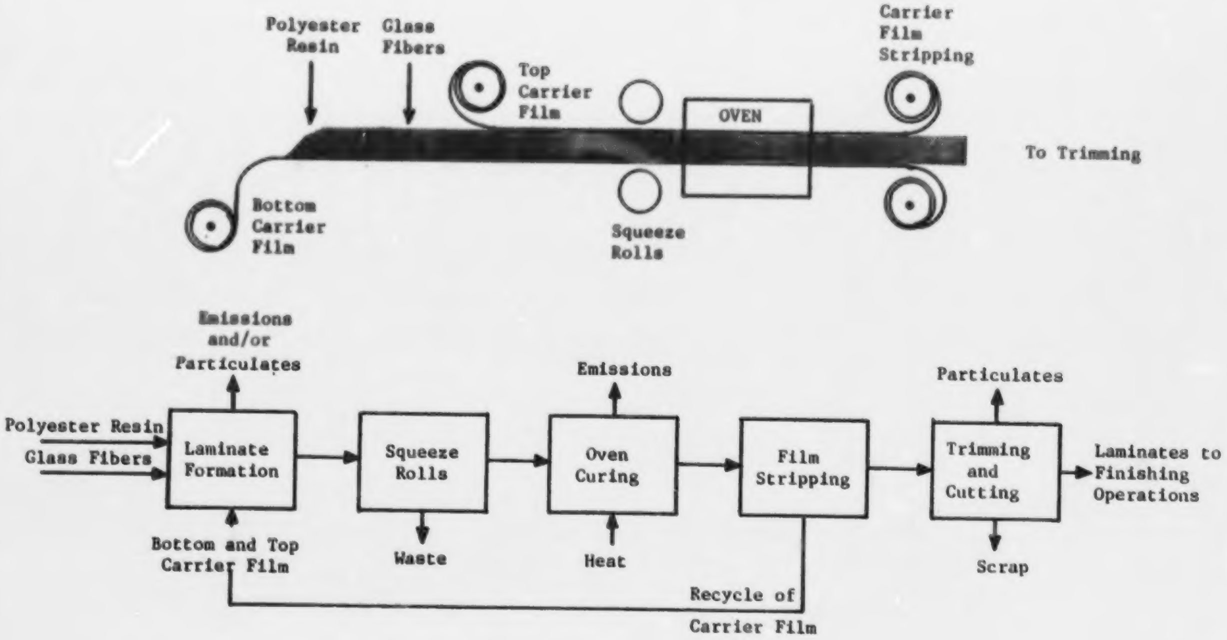
Polyester Resin
Glass Fibers
Top Carrier Film
OVEN
Carrier Film Stripping
To Trimming
Bottom Carrier Film
Squeeze Rolls
Emissions and/or Particulates
Polyester Resin
Glass Fibers
Laminate Formation
Bottom and Top Carrier Film
Squeeze Rolls
Waste
Emissions
Oven Curing
Heat
Film Stripping
Recycle of Carrier Film
Particulates
Trimming and Cutting
Scrap
Laminates to Finishing Operations

Figure 41. Continuous lamination.

OPERATING PARAMETERS AND UTILITY REQUIREMENTS

The actual temperatures and pressures used during laminating operations are highly dependent upon the resin being used and the product specifications. Laminating temperatures for flat laminate sheets range from 148 to 176°C.[10] Laminate rods and tubes are cured around 135°C.[59]

Laminating operations generally use high pressures; rarely lower than 6.8 x 10^6 Pa, and more commonly in the range of 8.2 to 13.8 x 10^6 Pa.[15]

WASTE STREAMS AND EMISSIONS

Laminating operations produce air emissions and solid waste. Wastewater is not directly generated by the laminating processes. Table 62 presents a summary of the point source emissions from laminating operations. Emissions and wastes for laminating are discussed in more detail below. The wastes and emissions from major plastics additives are discussed in more detail in the Industry Description section.

Air Emissions - Volatile emissions and particulates are generated during laminating operations. Particulates are generated during the handling of the fillers and other additives as they are combined with the resin to form the laminate. Particulates are also generated during the trimming and cutting of newly formed laminates. Such particulates would consist of fine particles of resin, additives and fillers and would be controlled by baghouse technology or wet scrubbing. When asbestos is used as a filler, particulate emissions could be harmful to worker health and safety.

Volatile emissions may occur during the application of resin to the filler and during heating and curing of the thermoset resins. These emissions may contain volatilized monomers, volatilized additives, and cure reaction by-products. Frequently resins are applied to the filler in a carrier solvent. The solvent is evaporated before the lamination process. Solvents may also be included in volatile emissions. Decomposition products are generally not formed since the temperatures used during laminating are not high enough to cause decomposition of the polymer.

Solid Waste - Plastic scrap is produced by the trimming and cutting of laminate sheets, rods, and tubes and from the collection of particulates. Such thermoset scrap cannot be recycled and must be disposed of as scrap. No problems should be presented by the disposal of the characteristically inert plastic.

WORKER DISTRIBUTION AND EXPOSURE

Plastics laminating operations are relatively simple. Worker distribution for laminating is similar to that for calendering operations. Estimated worker distribution for each of the three major laminating processes, determined by correlating equipment manhour requirements with the process flow diagrams in Figures 39 through 41, is shown in Table 63.

TABLE 62. LAMINATING POINT SOURCE EMISSIONS

	Air Emissions							Solid Waste		
	Volatiles				Particulates					
	Monomer	Solvent	Additives	Cure Reaction By-Products	Resin	Additives	Fibers	Resin	Additives	Fibers
Flat Laminate Sheets										
Loading and Closing	X	X	X							
Heating	X	X	X	X						
Trimming					X	X	X	X	X	X
Laminate Rods and Tubes										
Mandrel Winding	X		X							
Compression Mold	X		X	X						
Trimming					X	X	X	X	X	X
Continuous Lamination										
Laminate Formation	X		X			X	X			
Oven Curing	X		X	X						
Trimming					X	X	X	X	X	X

TABLE 63. WORKER DISTRIBUTION ESTIMATES FOR PLASTICS LAMINATING

Unit	Workers/Unit/8-hour Shift
Flat Sheets:	
Loading/Pressing	0.5
Cooling/Removal	0.5
Trimming	0.25
Rods and Tubes:	
Mandrel Winding/Removal	0.5
Molding	0.5
Trimming	0.25
Continuous Lamination:	
Laminate Rolling	0.5
Curing	0.25
Film Stripping	0.25
Trimming and Cutting	0.25

Employees in laminating operations may be exposed to gaseous emissions from laminate loading, heating and curing, and particulate emissions from sheet trimming. Release points and emissions from plastics laminating have been estimated from the literature and are shown in Table 64.

Little data are available in the literature from which employee exposure potential may be estimated. However, one source estimates hydrocarbon emissions from polyester laminating operations at 28-53 g/kg product.

Toxicity information for the contaminants in Table 64 is summarized in Appendix C of this document and discussed in depth in IPPEU Chapters 10 and 10b.

TABLE 64. PLASTICS LAMINATING EMISSIONS AND RELEASE POINT ESTIMATION

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Flat Sheet Production:		
Press Opening/ Closing	Fugitives	Volatile Monomer - formaldehyde - urea - melamine - epichlorohydrin - bisphenol-A - ethylene oxide - phenol - vinylidene chloride
		Volatile Solvent
		[1]Volatile Additives - decabromodiphenyl oxide - chlorinated paraffin wax
Heating/Curing	Fugitives	Volatile Monomer
		Volatile Solvent
		[1]Volatile Additives
		[2]Volatile Cure By-Products
Trimming	Fugitives	Polymer Particulates - alkyds - amino resins - epoxies - polyacetals - phenolics - polyvinylidene chloride

(continued)

TABLE 64 (continued)

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Trimming (cont.)	Fugitives (cont.)	Additive Particulates: Colorants - titanium dioxide Flame Retardants - antimony oxide - alumina trihydrate - decabromodiphenyl oxide - chlorinated paraffin wax Reinforcers - glass fibers - asbestos
	Trimming Tools	Noise
Rod and Tube Production:		
Mandrel Winding	Fugitives	Volatile Monomer
		[1]Volatile Additives
Compression Molding	Mold Vent Fugitives	Volatile Monomer
		[1]Volatile Additives
		[2]Volatile Cure By-Products

(continued)

TABLE 64 (continued)

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Trimming	Fugitives	Polymer Particulates
		Additive Particulates
	Trimming Tools	Noise
Continuous Lamination:		
Laminate Formation	Fugitives	Volatile Monomer
		Volatile Additives
	Lamination Rollers	Noise
Oven Curing	Fugitives	Volatile Monomer
		Volatile Additives
		[2]Volatile Cure By-Products
Trimming	Fugitives	Polymer Particulates
		Additive Particulates
	Trimming Tools	Noise

[1] Additives listed are documented in the literature. Many other additives may be used, depending on product formulation specifications.
[2] Not specified in literature.

MOLDING

Molding is the most common method utilized for producing finished or semi-finished products from plastic resins. Molded parts can be solid, hollow, or foamed materials. The production of foamed products is discussed in detail in the Foam section of this chapter.

Plastic objects of almost any desired shape can be produced commercially by six different types of molding processes:

- blow molding,
- compression molding,
- injection molding,
- reaction injection molding,
- rotational molding, and
- transfer molding.

The selection of the molding process for a given part depends on the properties of the resin being processed, part geometry, and the cost to produce a given number of units. The processing of thermoset plastics is considerably different than that of thermoplastics. In general, thermoplastics are processed by way of injection molding, blow molding, rotational molding, and reaction injection molding. Thermosets are processed by injection molding, transfer molding, and compression molding.

In almost all molding operations, pressure and heat must be applied to make the polymer take the desired product form. For the proper dimensional stability, thermoplastics have to be cooled before being removed from the mold, whereas thermosets require heat for a stable network structure to develop. Thermosets are often ejected from the mold while the polymer is still hot.

SECTION 13

BLOW MOLDING

FUNCTION

Blow molding is used to produce hollow, thin wall objects from thermoplastic resins. In recent years blow molding has become one of the major processing methods of the plastics industry for hollow articles. It can now successfully combine high-speed production with unique product design possibilities.

Blow molding allows for articles of thin and medium wall construction, but is impractical for heavy walls (above 0.32 cm).[191] Blow molding is also characterized by a lack of control over the inside dimensions of the molded article. This variability is generally not a problem in bottles and containers, but it makes blow molding impractical for technical applications requiring precision dimensions. Such items are usually manufactured by injection molding.

In comparison to injection molding, equipment costs for blow molding are generally lower for comparable production rates. The pressure used in blow molding is considerably lower than that required for injection molding and, therefore, lower internal stresses result in blow molded items.

INPUT MATERIALS AND PRODUCTS

Most thermoplastic materials can be blow molded if a formulation with a suitable melt viscosity is chosen. Of all plastic materials, high density polyethylene has traditionally been the workhorse of the blow molding industry. In recent years, the thermoplastic polymers listed below have been commercially used for blow molding:

- Acrylic Resins
- Acrylonitrile-Butadiene-Styrene (ABS)
- Polyacetal
- Polycarbonate
- Polyethylene Terephthalate (PET)
- Polyethylene
  - Low Density (LDPE)
  - High Density (HDPE)
  - Linear Low Density (LLDPE)
- Polypropylene
- Polystyrene
- Polyvinyl Chloride (PVC)

The formulation of polymers for blow molding processes is very important. The additivies are carefully chosen by processors to create the desirable characteristics in the polymer melt and blow molded product. Blow molding grades of input polymers can often be purchased directly from the polymer producer. The processor then completes formulation by adding the colorants and other additives specifically chosen for the product application. Additive "recipes" are specifically designed for each product and are usually considered proprietary information by processors. Table 65 delineates polymers, generalized formulations and products of the blow molding process. More detailed information on major plastics additives used in blow molding is presented in the Industry Description section of this document.

Two examples of formulations for blow-molding PVC bottles are shown below:[158]

Material	Parts by Weight Fruit-Squash Bottle Compound	 High-Clarity, High-Impact Compound
PVC Resin (Corvic D50/16)	100	100
Impact Modifier (Kane Ace B.12)	11	14
Stabilizer	(Stanclere 80) 2.2	(Mellite 831) 1
α-Phenyl Indole (stabilizer)	0.6	
Epoxidized Oil (Paraplex G62)	2.8	0.2
Lubricant (Estol 294)	1.1	
Wax Lubricant	1.1	0.1

Blow molding operations are used to produce a wide range of hollow bottles and containers. Around 80 percent of all blow molding operations are used to produce packaging items. These include household bottles and containers for cosmetics, toiletries, pharmaceuticals, chemicals, and foods, as well as industrial containers. The remaining 20 percent are used to produce industrial products such as automobile fuel tanks, lighting fixture globes, ornaments, and toys.[178]

PROCESS DESCRIPTION

Blow molding processes now in commercial use in the United States can be divided into two major categories: extrusion blow molding and injection blow molding. These two processes are similar in that they both utilize a preformed mass of plastic which has been shaped to have characteristics which will best suit the product specifications. This preformed mass of plastic is termed a parison and it is expanded by air pressure to fill the inside of a concave mold. The difference between extrusion blow molding and injection blow molding lies in the formation of the parison. Extrusion blow molding uses an extruder to form parisons shaped as cylinders whereas injection blow molding uses an injection molder. A detailed description of these two processes follows.

Extrusion Blow Molding - Extrusion blow molding is a continuous blow molding process capable of high production rates. A block diagram of extrusion blow molding is shown in Figure 42.

Polymer powder or pellets, colorants, and other additives are fed to a rotating screw extruder where they are mixed and heated into a homogeneous melt. The extrusion process is described in more detail in Section 6 - Extrusion. The plastic melt is forced through a die, which forms the plastic

TABLE 65. BLOW MOLDING INPUT MATERIALS AND PRODUCTS

Polymer	Formulation	Products
Acrylic Resins	UV Stabilizers Colorants	Small hollow parts Aerosol and carburator floats Bottles
ABS	Resin must be dried 2-4 hours at 82-93°C (180-220°F) in a dehumidifying, circulating, air hopper dryer	Household chemical bottles Detergent bottles Mouthwash bottles Pharmaceutical bottles Food and beverage bottles
Polyacetal	Colorants Flame Retardants UV Absorbers	Bottles for aerosol sprays Other containers
	Colorants UV Stabilizers Antioxidants	Bottles for aerosol sprays Other containers
Polycarbonate	Resin must be dried at 127°C (260°F) in dehumidifying hopper dryer Colorants Flame Retardants UV Stabilizers	Returnable milk and water bottles Lighting globes Baby bottles Medicinal and health packaging Toiletry bottles Floor polish bottles Mineral oil bottles Liquor bottles
Polyester (PET)	Dried for 4 hours at 66-71°C (150-160°F) Glycol Modifiers Colorants	Half liter beverage bottles Soft drinks bottles Shampoo bottles Detergent bottles Other bottles
Polyethylene		
LDPE	Antiblocking Agents Antioxidants Antistatic Agents Colorants UV Stabilizers	Milk bottles Bleach bottles Household containers Squeeze bottles Industrial chemical bottles Pails Drums

(continued)

TABLE 65 (continued)

Polymer	Formulation	Products
Polyethylene (Continued)		
HDPE	Antiblocking Agents Antioxidants Antistatic Agents Colorants Flame Retardants Impact Modifiers UV Stabilizers	Emulsion type polish bottles Liquid starch bottles Fabric softener bottles Bleach bottles Detergent bottles Swimming pool chemical bottles Milk bottles Antifreeze bottles Pharmaceutical bottles Motor oil bottles Vitamin bottles Fuel tanks for trucks and buses Housewares Shampoo bottles Milk of magnesia bottles Scented talc bottles Large drums Pails Toys
LLDPE	Antioxidants Stabilizers Colorants UV Stabilizers	Assorted bottles Toys Drum liners
Polypropylene	Antiblocking Agents Antioxidants Antistatic Agents Colorants Plasticizers	Medical containers Household detergent Shampoo bottles Pancake syrup bottles Pharmaceutical bottles Fruit drink bottles Milk bottles Bleach bottles Cleanser bottles Washing machine liners
Polystyrene	Rubber modified impact resin with: Antistatic Agents Colorants Flame Retardants UV Inhibitors	Assorted bottles Cosmetic containers Display figures Furniture Toys Decorative products

(continued)

TABLE 65 (continued)

Polymer	Formulation	Products
PVC	Flexible and rigid resins with: Colorants Heat Stabilizers Impact Modifiers Lubricants Plasticizers	Food and beverage bottles Shampoo bottles Talcum powder bottles Car-care product bottles Baby bottles Detergent bottles Toiletry bottles Oil bottles

Sources: Agranoff, J.(ed). *Modern Plastics Encyclopedia 1981-1982*, pp. 4, 5, 8, 46, 50, 58, 80, 90, and 100.

Brown, R., *Design and Manufacture of Plastic Parts*, 1980, p. 84.

Dadik, Sandra and Marilyn Bakker, *Blow Molding Enters the Eighties*, 1979, p. 2-28.

Gaylord, Norman G. (ed). *Encyclopedia of Polymer Science and Technology*, 1968, Vol. 1, p. 440.

Fisher, Edwin George, *Blow Molding of Plastics*, 1971, pp. 143-163.

Glanville, A. B., *The Plastic Engineer Data Book*, 1973, p. 122.

Grayson, Martin (ed). *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 16, pp. 466, 397, 448, 417-420.

Penn, W. S., *PVC Technology*, 1971, p. 317.

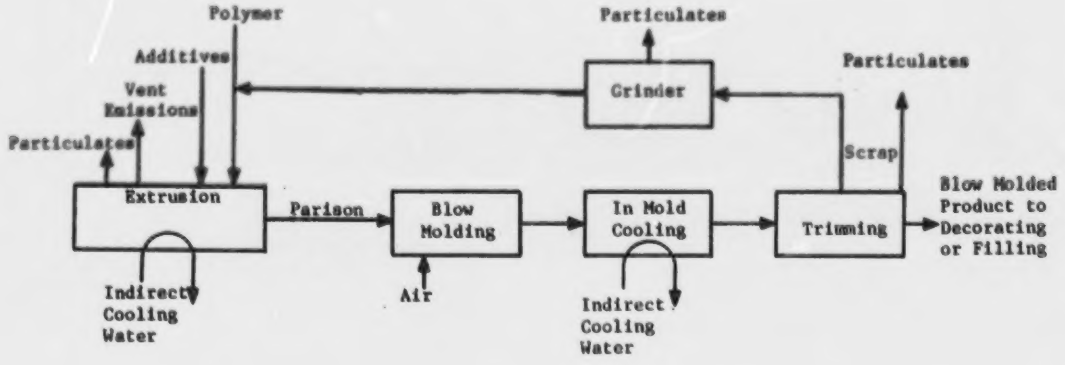
Polymer
Additives
Vent Emissions
Particulates
Extrusion
Indirect Cooling Water
Parison
Blow Molding
Air
In Mold Cooling
Indirect Cooling Water
Trimming
Blow Molded Product to Decorating or Filling
Scrap
Particulates
Grinder
Particulates

Figure 42. Extrusion blow molding.

into a parison shaped as a cylindrical tube. The actual size and shape of the tube is determined by the requirements of the final product. As the parison is extruded through the die it is positioned between the open halves of a concave mold. The mold halves are clamped together hydraulically. The clamping action pinches the tube together on the bottom and pinches off the top of the tube from the extruder feed. When bottles are being molded, the top of the mold is designed to form the threads in the neck area of the bottle. Compressed air is introduced into the parison by a blow pin at the top or hypodermic needles in the bottom. The air pressure forces the parison to conform to the inner shape of the mold. The mold halves are cooled by indirect cooling water or other means thereby solidifying the blown melt into its final product shape. When the part has sufficiently cooled to hold the desired shape, the mold halves open, and the part is stripped from the mold by air blasts or mechanical ejector pins.

Extrusion blow molded products have flash on the ends where the parison was pinched off. This flash can be removed manually or by automatic trimmers. Trim and defective containers can usually be ground and recycled to the polymer feed of the extruder. The blow molded product then proceeds to decorating, labelling, or filling operations.

Most extrusion blow molding operations are performed in a rotary set up. A parison is extruded into a mold at the first station. The mold then rotates to the second station where the part is blown. At the third and fourth stations the part cools and is ejected. The mold halves return to station one to receive a newly extruded parison. This rotary setup allows for continuous extrusion of parisons and highest possible production rates from the blow molding system.

Injection Blow Molding - Injection blow molding is a two stage process for producing plastic containers which require no trimming. A block diagram of injection blow molding is shown in Figure 43.

In the first stage of injection blow molding a parison is formed by way of injection molding. The injection molding process is described in detail in Section 15 - Injection Molding. During the injection molding of parisons the plastic melt is injected around a core pin in a preform mold. The parison is kept at its melt temperature in order to maintain its pliability for the subsequent blowing stages. The preform mold is designed to produce parisons which will produce the best blow molded products. In the case of bottle production, the parison has a fully shaped threaded neck and a closed end.

The parison is transferred by way of the core pin to the blow mold. In this second stage, air is blown through the core pin forcing the parison to take the shape of the mold. The mold halves are usually cooled by indirect cooling water in order to remove heat from the product. When the part is cooled it is removed from the mold and is ejected from the core pin.

Injection blow molded products do not require trimming and therefore produce no plastic scrap. Such products are completely finished when ejected from the blow molder and proceed directly to decorating, labelling, or filling operations.

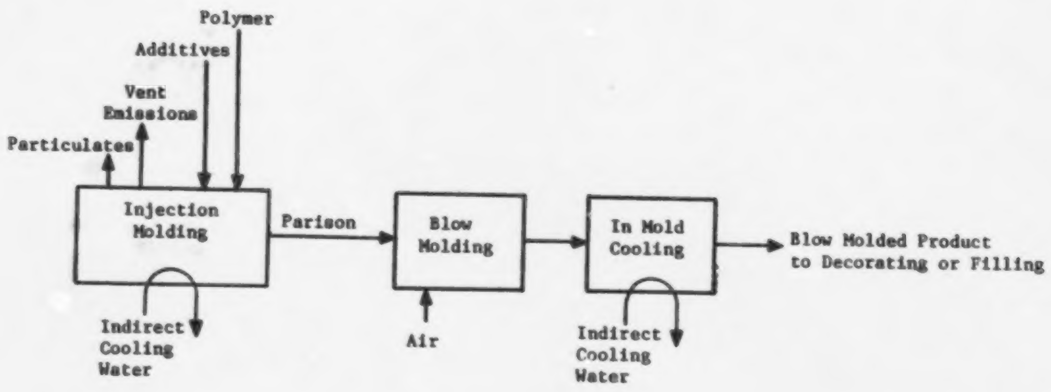
Polymer
Additives
Vent Emissions
Particulates
Injection Molding
Parison
Blow Molding
In Mold Cooling
Blow Molded Product to Decorating or Filling
Indirect Cooling Water
Air
Indirect Cooling Water

Figure 43. Injection blow molding.

In some operations the injection molding of the parison and the blow molding of the product do not follow immediately after one another. The injection molded parisions can be stored for later blow molding, in which case they are reheated in reflective radiant heat or quartz electrical heaters prior to being blow molded.

OPERATING PARAMETERS AND UTILITY REQUIREMENTS

As in most polymer processing operations, the operating conditions and utility requirements are highly governed by the polymer being processed and the desired end product. Most processors use resin producer's guidelines to determine rough settings for the temperatures, pressures, and speeds used in the parison formation and blow molding operations. The process is then fine tuned by trial and error to determine the optimum temperatures and pressures. Cooling and heating requirements are then determined to maintain the necessary operating parameters.

The melt temperatures, mold temperatures, and blowing pressures shown in Table 66 are typical of those required for blow molding.

Blow molding operations utilize cooling water to run through the cooling chambers of the mold halves, thereby cooling the polymer part to shape retention.

Hydraulic energy is utilized to open and close mold halves. In overall energy consumption, multi-stage blow molding machines exhibit considerably less energy consumption than the single-stage machines.

WASTE STREAMS AND EMISSIONS

Blow molding operations produce air emissions and solid waste. No wastewater is produced since water is used only in the indirect cooling of the mold halves. Table 67 presents a summary of the point source emissions from blow molding operations. The waste streams and emissions from major plastics additives utilized in blow molding are detailed in the Industry Description section of this document.

Air Emissions - Both extrusion and injection blow molding operations have the potential to produce particulate and hydrocarbon emissions. Particulates are produced from the polymer feed and mixing during the extrusion and injection molding segments of blow molding. Particulates are also produced by the trimming and subsequent grinding of extrusion blow molded product flash. These particulates consist of particles of polymer and additives. Most of the particulates and emissions produced are due to the extrusion and injection molding segments of the operation and not the actual blow molding segment.

Volatile emissions are liberated from extruder barrel vents and injection molder cylinders. These emissions consist of traces of monomers, additives, and decomposition products. Decomposition products occur when the processing temperature reaches that temperature at which the polymer begins to decompose. Table 68 presents those decomposition products which could be formed during blow molding operations.

TABLE 66. BLOW MOLDING TEMPERATURES AND PRESSURES

Polymer	Melt Temperature (°C)	Blow Mold Temperature (°C)	Blowing Pressure (Pax10^5)
Acetal	193 - 216	93 - 149	6.9 - 10.0
Acrylic	205 - 232	93 - 104	5.5
ABS	199 - 204	93 - 104	2.7 - 6.9
Polycarbonate	260 - 282	82 - 93	6.9
Polyester (PET)	270 - 300	2 - 54	5.5 - 6.9
Polyethylene			
LDPE	140 - 160	4 - 21	3.4
HDPE	170 - 190	4 - 21	5.5
LLDPE	170 - 199	4 - 21	5.5
Polypropylene	190 - 220	4 - 21	5.2 - 6.9
Polystyrene	185 - 230	66 - 93	2.7 - 6.9
PVC	150 - 180	10 - 21	5.2 - 6.9

Sources: Agranoff, J. (ed). Modern Plastics Encyclopedia 1981- 1982, pp. 4, 5, 8, 46, 50, 58, 80, 90, and 100.

Glanvill, A. B., The Plastics Engineer Data Book, 1973, p. 122.

TABLE 67. BLOW MOLDING POINT SOURCE EMISSIONS

	Air Emissions					Solid Waste	
	Particulates		Volatiles				
	Polymer	Additives	Monomer	Additives	Decomposition Products	Polymer	Additives
Extrusion Blow Molding							
Extruder	X	X	X	X	X		
Trimming	X	X				X	X
Grinder	X	X					
Injection Blow Molding							
Injection Molder	X	X	X	X	X		

TABLE 68. DECOMPOSITION PRODUCTS

Polymer	Highest Processing Temperature (°C)†	Decomposition Temperature (°C)§	Decomposition Products
ABS	204	300	*
Acrylic Resins	232	320	*
Polyacetal	216	250	*
Polycarbonate	282	330	*
Polyester (PET)	300	300	acetaldehyde
Polyethylene	190	100	Ketone carbonyl groups form due to oxidation
Polypropylene	220	300	*
Polystyrene	230	300	*
PVC	180	100	HCl

---

*Decomposition products are not formed at or near blow molding temperatures.

†This is the highest possible temperature reached by the normal blow molding of all formulations of the polymer listed.

§This is the lowest temperature at which decomposition products begin to form.

Solid Waste - Thermoplastic scrap generated by the trimming of extrusion blow molded product flash can usually be ground and recycled to the extruder feed. Excess scrap and particulates which cannot be recycled must be disposed of as solid waste. Since this waste is comprised of primarily inert plastic material, it will pose no disposal problems.

WORKER DISTRIBUTION AND EXPOSURE

Manpower requirements for extrusion and injection blow moldings are similar. We have estimated worker distribution for each by correlating major equipment manhour requirements with the process flow diagrams in Figures 42 and 43. Use of pre-formed parisons in injection blow molding will reduce manpower requirements for this process. Worker distribution estimates are shown below in Table 69.

Emissions from blow molding operations are similar to those in extrusion operations. Particulate and gaseous emissions may be present in both extrusion and injection blow molding. Table 70 lists potential contaminants and probable release points from each process.

Toxicity information for the contaminants listed in Table 70 is given in Appendix C of this document and in IPPEU Chapters 10 and 10b.

TABLE 69. WORKER DISTRIBUTION ESTIMATES FOR BLOW MOLDING PROCESSES

Unit	Workers/Unit/8-hour Shift
Extrusion Blow Molding	
Extrusion	0.5
Molding	0.5
Cooling	0.125
Trimming	0.25
Injection Blow Molding	
Injection Molding (parison formation)	1.0
Blow Molding	0.5

TABLE 70. BLOW MOLDING EMISSIONS AND RELEASE POINT ESTIMATION

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Extrusion Blow Molding		
Extruder	Fugitives	[1]Polymer Particulates - polyethylenes - acrylics - ABS - polyacetal - polycarbonate - polybutylene terephthalate - polyethylene terephthalate - polypropylene - polystyrene - polyvinyl chloride
		[2]Additive Particulates: Antioxidants - BHT - trisnonylphenyl phosphite - dilauryl thiodipropionate- Flame Retardants - antimony oxide - decabromodiphenyl oxide - chlorinated paraffin wax Heat Stabilizers - Ca/Zn stearate

(continued)

TABLE 70 (continued)

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Extruder (continued)		Volatile Additives
		Decomposition Products - acetaldehyde (from polyethylene terephthalate) - ketone carbonyls (from polyethylene) - HCl (from polyvinyl chloride)
		[3]Volatile Monomer - methyl methacrylate - 1-3, butadiene - acrylonitrile - styrene - formaldehyde - bisphenol-A - ethylene glycol - dimethyl terephthalate - terephthalic acid - 1,4-butanediol - propylene - vinyl chloride monomer
Trimming	Fugitives	[1]Polymer Particulates
		[2]Additive Particulates
	Trimming Tools	Noise

(continued)

TABLE 70 (continued)

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Scrap Grinding	Fugitives	[1]Polymer Particulates
		[2]Additive Particulates
	Grinders	Noise
Injection Blow Molding		
Injection Molding	Mold Vents Fugitives	[1]Polymer Particulates
		[2]Additive Particulates
		[3]Volatile Monomer
		Volatile Additives
		Decomposition Products

[1] Polyethylene is most commonly blow-molded, but small quantities of other polymers listed may be commercially blow-molded.

[2] Major additives documented in the literature. Other additives may also be present.

[3] Principal monomers used in polymers typically blow-molded. Other monomers or comonomers may be used.

SECTION 14

COMPRESSION MOLDING

FUNCTION

Compression molding is one of the earliest forms of molding, dating back as far as the 1860's. It was the predecessor of both injection molding and transfer molding and requires only one major piece of rugged equipment: the compression press.[136]

Compression molding is primarily used for processing thermoset resins, although it is used to mold thermoplastics for special applications. Compression molding of thermoplastics is not economically competitive with injection molding because of the lengthy cool-down times required during thermoplastic compression molding.

Compression molding involves shaping a measured quantity of plastic within a mold by applying pressure and heat. This molding process is ideal for the production of parts with large areas which have relatively simple shapes. It is slow compared to other molding processes and compression molded parts sometimes require extensive finishing.

INPUT MATERIALS AND END PRODUCTS

Resins utilized for compression molding are available from the producer in fine powders, granules, and flakes. Commonly used formulations are also available as premeasured preforms, tablets, or slugs of polymer. The majority of polymers which are compression molded are thermoset resins. Smaller volumes of thermoplastics are compression molded for special applications. Polymers which are most commonly compression molded include:

- Alkyd Resins
- Amino Resins
  - Melamine Formaldehyde
  - Urea Formaldehyde
- Diallyl Phthalate (DAP)
- Epoxy Resins
- Phenolic Resins
- Polyester Resins

Other less frequently compression molded polymers include:

- Acrylic Resins
- Acrylonitrile-Butadiene-Sytrene (ABS)
- Engineering Thermoplastics
- Fluoropolymers
- Polyacetal
- Polyamide
- Polybutylene
- Polycarbonate
- Polyurethane
- Polyvinyl Chloride (PVC)
- Polyvinylidene Chloride
- Styrene-Acrylonitrile

Fillers are often used during compression molding to give the finished product the desired properties and strength. Fillers and other additives used with commonly compression molded thermosets are shown in Table 71. Table 72 presents a list of typical products produced by compression molding operations. More detailed information on major plastics additives is presented in the Industry Description section of this document.

Several examples of compression molding formulations are given below.

A typical brake lining formula, based on phenolic resins, is given below:[187]

Material	Parts by Weight
Phenolic Resin	25
Asbestos (filler)	60
Brass (friction modifier)	15

A typical formulation for a general-purpose compound, suitable for compression molding, is as follows:[109]

Material	Parts by Weight
Novolac Resin	100
Hexamethylenetetramine (cross-linking agent)	12.5
Wood Flour (filler)	110
Lime (filler)	2
Stearic Acid	2
Nigrosine (colorant)	2

A typical polyester molding compound formula, suitable for heater housings, wash basins, and shower stalls, is given below:[187]

Material	Parts by Weight
General Purpose Polyester (with 20% styrene)	30-35
Benzoyl Peroxide (catalyst)	0.5
Zinc Stearate (lubricant)	1.2
TiO_2 (whitener)	1.5
Marble Dust (filler)	40-60
Asbestos (fiber)	10-20

A typical formulation for a sheet molding compound, based on unsaturated polyester resin and chopped glass roving, is shown below:[74]

Material	Parts by Weight
Unsaturated Polyester Resin	100
Low Profile/Low Shrink Thermoplastic Additive	43-67
Precipitated Calcium Carbonate (filler)	150-250
Magnesium Oxide or Hydroxide	2.5-3.0
Zinc Stearate (lubricant)	3-4
Chopped Glass Roving (filler)	100-140

TABLE 71. COMMONLY USED COMPRESSION MOLDED FILLERS AND OTHER ADDITIVES

		Alkyd	Diallyl Phthalate	Epoxy	Melamine-Formaldehyde	Phenolic	Urea-Formaldehyde
Fillers	Asbestos		X		X	X	
	Cellulose				X		X
	Cotton					X	
	Glass Balloons			X		X	
	Glass Fiber	X	X	X	X	X	
	Mica					X	
	Mineral		X	X	X	X	
	Rubber					X	
	Silica					X	
	Sisal					X	
	Synthetic Fiber		X	X			
	Wood Flour				X	X	X
Other Additives	Catalysts				X		X
	Colorants	X	X		X	X	X
	Cure Agents		X	X		X	
	Crosslinking Agents		X				
	Flame Retardants	X		X			
	Inhibitors		X				
	Lubricants		X		X		X
	Promoters		X				
	Stabilizers				X		X

TABLE 72. TYPICAL COMPRESSION MOLDED PRODUCTS

Appliance Bases - Mixers and Coffee Pots
Ash Trays
Audio Records
Battery Cases
Bottle Caps and Closures
Buttons
Camera Cases
Cams, Gears, and Pulleys
Can Opener Fronts
Carburetor Spacers
Circuit Breakers
Coil Towers
Dinnerware: Plates and Bowls
Distributor Caps
Door Mats
Electrical and Electronic Components
Fresnel Lenses
Fuse Blocks
Gaskets, Grommets, and Stoppers
Heater Bases
Ignition Parts
Impellers
Instrument Housings
Knobs and Handles
Lamp Housings
Missile Components
Outlet Boxes
Pipe Fittings
Pot Handles
Power Brakes and Transmission Components
Pump Housings
Rocket Nozzles
Rotors
Shoe Heels
Slabs to be Machined into Intricate Parts
Solenoid Covers and Housings
Timing Motor Housings
Terminal Boxes
Valves
Wall Switch Plates
Washing Machine Agitators

PROCESS DESCRIPTION

Unless preformulated preforms are purchased by the processor, input materials for compression molding such as the resin, fillers, colorants, and lubricants must be blended prior to their use in the compression molding process. Often the blended material is formed into a preform of specific weight prior to its use. A more detailed description of blending methods can be found in the formulation section of this document.

As shown in Figure 44, the plastic material is fed to the compression mold either in granular form or as a preform. The material can be at ambient temperature or it can be preheated. Most compression molding operations which preheat use a radio frequency unit to preheat preforms to 93 to 143°C.[70] Granules are heated to similar temperatures using infrared rays.[70]

Premeasured amounts of material are fed to the mold either manually or automatically. The material weight allows for part requirements and for flash.

Once the material is in the mold, the mold halves are closed by a hydraulic press. The pressure is maintained and heat is applied, causing the plastic to spread to the shape of the mold. Vents in the mold allow trapped air and gas to escape. For thermoset processing, the heat is maintained until the part has sufficiently cured for removal. Thermoset parts can usually be removed while the mold is still hot and a new charge of material is immediately placed in the mold. Thermoplastic parts are removed from the mold when they are cool thereby requiring much longer cycle times than thermosets.

The hydraulic press opens the mold halves and the part is removed by mechanical ejector pins. In the production of extremely large parts, part removal is often performed manually.

Compression molded parts must be trimmed in order to remove flash at the mold parting line. Parts are then finished by machining, buffing, or polishing to produce the desired shape or surface finish.

Compression molds can have single or multiple cavities. The design of these molds must allow for the shrinkage exhibited by the polymer during curing or cooling. The amount of shrinkage to be expected is dependent upon the polymer and filler used. Shrinkage generally ranges from 0.05 to 0.9 percent by area.[76] Heat transfer must also be carefully considered in compression mold design. If the mold is improperly designed, the mass will become rigid on the outside while still molten on the interior, causing stress within the part. Most molds are designed to have mold faces with large areas to allow for even heat transfer, along with sufficient channels within the mold for heating or cooling fluid circulation.

OPERATING PARAMETERS AND UTILITY REQUIREMENTS

The polymer formulation and the configuration of the part must be taken into consideration when determining what the molding temperature and pressure should be. Thin-wall sections are generally molded at the upper end of the

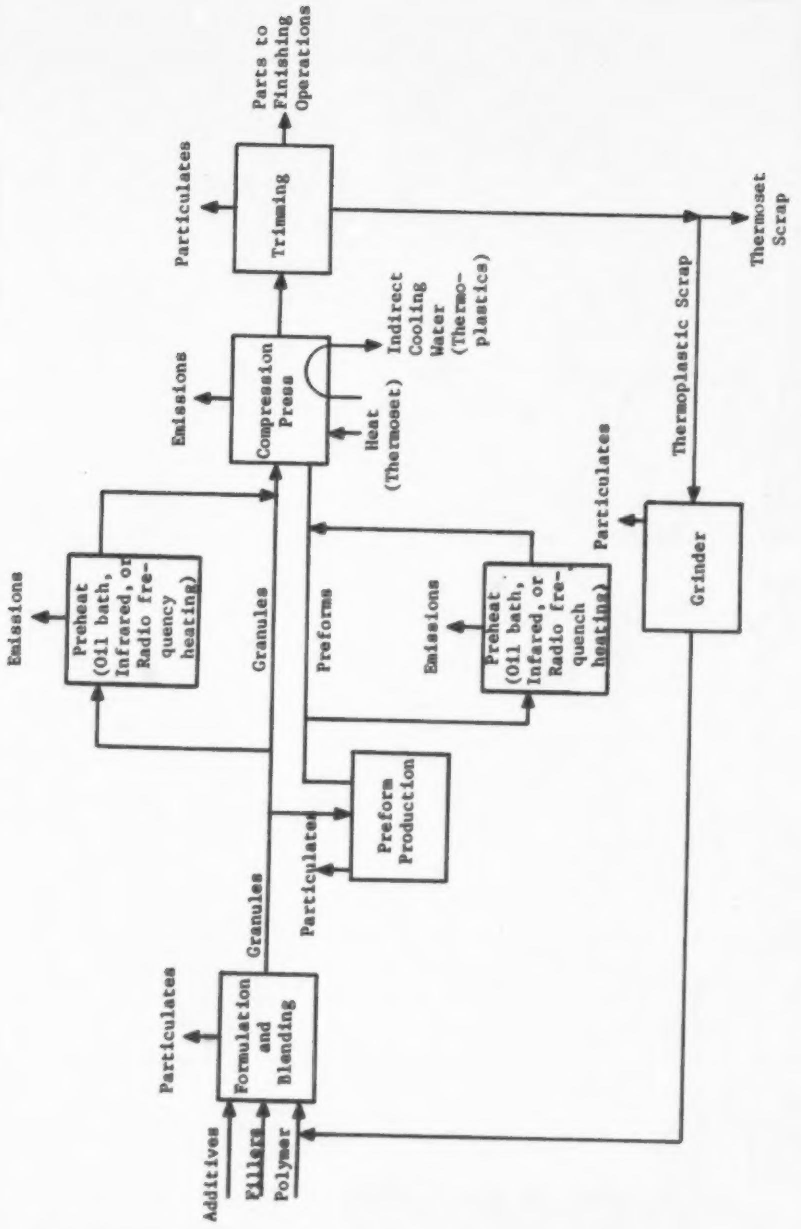
Additives
Fillers
Polymer
Formulation and Blending
Particulates
Granules
Particulates
Preform Production
Granules
Preheat (Oil bath, Infrared, or Radio frequency heating)
Emissions
Preforms
Preheat (Oil bath, Infared, or Radio frequench heating)
Emissions
Compression Press
Emissions
Heat (Thermoset)
Indirect Cooling Water (Thermoplastics)
Trimming
Particulates
Parts to Finishing Operations
Thermoset Scrap
Thermoplastic Scrap
Grinder
Particulates

Figure 44. Compression molding.

temperature/pressure range while thick-wall sections are molded at the lower end. A product with both thick- and thin-wall sections is molded in the low-to-middle range. Table 73 presents typical compression molding temperatures and pressures.

In compression molding operations, the temperature and pressure are estimated and the actual parameters are then determined through trial runs. Cycle times in compression molding typically range from 0.5 to 8 minutes; with the exact time determined during the trial runs.[70]

The compression molding pressure is specified as the pressure exerted on the plastic material in the mold cavity. The pressure for compression molding is generally provided by hydraulic presses. Estimates of molding pressure must take into consideration the type of plastic, as well as the design and size of the part to be made. The heat for compression molds is generally supplied by steam or electricity and, in some cases, hot gas or oil. Heat is channeled as close to the mold cavity as possible to provide uniform heating across all mold surfaces. During thermoplastic molding, indirect cooling water is required to cool the part sufficiently such that it can be removed from the mold.

WASTE STREAMS AND EMISSIONS

Compression molding operations produce air emissions and solid waste. Table 74 presents a summary of the point source emissions which result from compression molding operations. More detailed information on waste streams and emissions resulting from major plastics additives used in compression molding is available in the Industry Description section of this document.

Air Emissions - Compression molding operations have the potential to produce particulate and hydrocarbon emissions. Particulates are produced from the polymer formulation, blending, and preform production. Particulates are also produced by the trimming of parts and the grinding of thermoplastic scrap. These particulates consist of particles of polymer, fillers, and other additives.

Volatile emissions are liberated during the preheating of granules and preforms, as well as during the actual compression cycle. Compression molds usually contain vents or have a designed clearance to allow for the release of gaseous emissions. During the molding of thermosets which produce gaseous by-products during their cure, the mold may actually be opened to allow them to escape. Volatile emissions liberated consist of traces of monomers, additives, cure reaction by-products, and decomposition products. Decomposition products occur when the processing temperature reaches that temperature at which the polymer begins to decompose. Table 75 presents those decomposition products which could be formed during compression molding operations.

Solid Waste - Thermoplastic scrap generated by the trimming of product flash can usually be ground and recycled to the formulation and blending step. Excess scrap and particulates, as well as trimmed thermoset scrap, must be disposed of as solid waste. Since this waste is comprised primarily of inert plastic material it will pose no disposal hazards.

TABLE 73. COMPRESSION MOLDING TEMPERATURES AND PRESSURES

Polymer	Temperature °C	Pressure (Pa x 10^7)
Acrylics	149 - 218	1.4 - 6.9
Alkyd Resins	121 - 165	0.4 - 1.7
Diallyl Phthalate	121 - 163	0.3 - 1.4
Epoxy Resins	143 - 180	0.7 - 1.4
Melamine Formaldehyde	138 - 177	1.4 - 5.5
Phenolic Resins	143 - 177	1.0 - 6.9
Polyester	82 - 149	0.03 - 0.3
PTFE	360 - 380	1.4 - 6.9
Polyurethane	218	0.7 - 5.5
PVC	177	0.7 - 5.5
Urea Formaldehyde	135 - 154	1.4 - 5.5

Sources: Baird, R. J., Industrial Plastics, 1971, p. 273.

Milby, R. V., Plastics Technology, 1973, p. 130.

Rodriguez, F., Principles of Polymer Systems, 1970, pp. 341-344.

Schwartz, Seymour S. and Sidney H. Goodman, Plastics Material and Processes, 1982, p. 168.

TABLE 74. COMPRESSION MOLDING POINT SOURCE EMISSIONS

	Air Emissions							Solid Waste		
	Particulates			Volatiles						
	Polymer	Filler	Additives	Cure Reaction By-Products	Monomer	Additives	Decomposition Products	Filler	Polymer	Additives
Formulation/Blending	X	X	X		X	X				
Preform Production	X	X	X							
Preheaters					X	X				
Compression Press				X	X	X	X			
Trimming and Grinding	X	X	X					X	X	X

TABLE 75. DECOMPOSITION PRODUCTS

Polymer	Highest Processing Temperature (°C)†	Decomposition Temperature (°C)§	Decomposition Products
Acrylics	218	320	*
Alkyd Resins	165	232	*
Diallyl Phthalate	163	225	*
Epoxy Resins	180	200	*
Melamine Formaldehyde	177	182	*
Phenolic Resins	177	300	*
Polyester	149	275	*
PTFE	380	300	HF
Polyurethane	218	300	*,#
PVC	177	100	HCl
Urea Formaldehyde	154	182	*

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*Decomposition products are not formed at or near compression molding temperatures.

†This is the highest possible temperature reached by the normal compression molding of all formulations of the polymer listed.

§This is the lowest temperature at which decomposition products begin to form.

#The presence of humidity at molding temperature may cause hydrolysis of the urethane functional groups.

WORKER DISTRIBUTION AND EXPOSURE

Compression molding operations are typically semiautomated. All but very large parts are mechanically removed from the mold. We have estimated worker distribution by correlating major equipment manhour requirements with the process flow diagram in Figure 44, as shown below:

Unit	Workers/Unit/8-hour Shift
Formulation/Blending	0.5
Preform Production (if employed)	0.5
Polymer Preheat	0.25
Molding	0.5
Trimming	0.25
Scrap Grinding (thermoplastics only)	0.25

Emissions from compression molding are similar to those discussed previously for other molding processes. Additionally, employees may be exposed to a variety of filler materials used to give finished products desired properties and strength.

Probable release points and contaminants, estimated from the literature, are shown in Table 76. Toxicity information for these contaminants is summarized in Appendix C of this document and discussed in detail in IPPEU Chapter 10 and 10b.

TABLE 76. COMPRESSION MOLDING EMISSIONS AND RELEASE POINT ESTIMATION

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Formulation/Blending (no preform production)	Fugitives	[1]Polymer Particulates - ABS
		- acrylics
		- engineering thermoplastics
		- fluoropolymers
		- polyacetals
		- polyamides
		- polyolefins
		- alkyds
		- amino resins
		- epoxies
		- phenolics
		- polyvinyl chloride
		- polyesters
		[2]Additive Particulates: Colorants - Cd sulfoselenide
		- phthalocyanines
		- monoazo yellow
		Flame Retardants - antimony oxide
		- alumina trihydrate
		Reinforcers - glass fibers
		- asbestos
		- silica

(continued)

TABLE 76 (continued)

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Formulation/Blending (continued)		[3]Filler Particulates: Alkyds - glass fiber Epoxies - glass balloons - glass fiber - mineral wool - synthetic fiber Melamine/Formaldehyde - asbestos - cellulose - glass fiber - mineral wool Phenolics - asbestos - cotton - glass balloons - glass fiber - mica - mineral wool - silica - sisal - wood flour Urea/Formaldehyde - cellulose - wood flour
		[4]Volatile Monomer - formaldehyde - urea or melamine - epichlorohydrin - bisphenol-A - chlorofluorocarbons - phenol - vinyl chloride
		Residual Volatile Additives

(continued)

TABLE 76 (continued)

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Preform Production	Fugitives	[1]Polymer Particulates
		[2]Additive Particulates
		[3]Filler Particulates
Preheaters	Fugitives	[4]Volatile Monomer
		Volatile Additives
	Preheater	Non-ionizing Radiation (radio frequency waves)
Compression Press	Mold Vents Fugitives	[4]Volatile Monomer
		Volatile Additives
		[5]Cure By-Products
		Decomposition Products - HF (fluorocarbons) - HCl (polyvinyl chloride)
Trimming and Scrap Grinding	Fugitives	[1]Polymer Particulates
		[2]Additive Particulates
		[3]Filler Particulates
	Trimming/Grinding Tools	Noise

[1] Polymers typically compression molded. Others may be compression molded for specialty applications.

[2,3] Specific additives and fillers listed are those documented in the literature. Many other additives and fillers may be used, depending on product specifications.

[4] Principal monomers used to produce polymers typically formed by compression molding. Other monomers or comonomers may be present.

[5] Unspecified.

SECTION 15

INJECTION MOLDING

FUNCTION

Injection molding is used for the formation of intricate plastic parts with excellent dimensional accuracy. A large number of items associated with our daily life are produced by way of injection molding. Typical product categories include housewares, toys, automotive parts, building supplies, and household furnishings.

Injection molding involves the plasticating of pelletized plastic with heat and the subsequent injection of the melt into a mold cavity. Most mold assemblies are comprised of multiple cavities thereby allowing for very high production rates. The high production rates make injection molding a very economical method for producing plastics products.

INPUT MATERIALS AND PRODUCTS

Both thermoplastic and thermoset polymers are injection molded. The majority of injection molded products are produced from the polyethylenes, polypropylene, polystyrene, and acrylonitrile-butadiene-styrene (ABS). Alkyd resins and linear low density polyethylene are being injection molded for some specialty applications. The following is a list of those polymers which are now commercially injection molded:

Thermoplastics

- Acrylic Resins
- Acrylonitrile-Butadiene-Styrene (ABS)
- Fluoroplastics
  - Ethylene-Tetrafluoroethylene Copolymer (PTFE) (Teflon®)
  - Fluorinated Ethylene Propylene Copolymer (FEP) (Tefzel®)
  - Polyvinylidene Fluoride (PVDF) (Kynar®)
- Nylon 6
- Nylon 6/6
- Phenolic Resins
- Polyacetal
- Polybutylene
- Polycarbonate
- Polyester
  - Polybutylene Terephthalate (PBT)
  - Polyethylene Terephthalate (PET)
- Polyethylene
  - Low Density (LDPE)
  - High Density (HDPE)
  - Ethylene Vinyl Acetate (EVA)
- Polyphenylene Oxide
- Polyphenylene Sulfide
- Polypropylene
- Polystyrene
- Polyvinyl Chloride (PVC)
- Styrene-Acrylonitrile (SAN)
- Vinylidene Chloride

Thermosets

Diallyl Phthalate (DAP)
Melamine-Formaldehyde
Unsaturated Polyester Resins
Urea Formaldehyde

The polymer feed is usually in the form of small pellets or granules. The condition and size of the raw materials must be carefully controlled in order to avoid feed problems. Air entrapment and moisture must be avoided in order to prevent streaking and voids in the injection molded product. Some moisture sensitive polymers (i.e., ABS, Nylon, Polycarbonate, Polyester, and SAN) must be pre-dried.

The formulation of polymers for injection molding is very important. Additives are carefully chosen by processors to create the desirable characteristics in the polymer melt and the final molded product. Injection molding grades of input polymers can often be purchased directly from the polymer producer. The processor then completes formulation by adding the colorants and other additives specifically chosen for the product application. Additive "recipes" are specifically designed for each product and are usually considered proprietary information by processors. Table 77 delineates polymers, generalized formulations, and products of injection molding. More extensive information on major plastics additives utilized in injection molding is detailed in the Industry Description section of this document.

A typical formulation for an ethylene-vinyl acetate resin for injection molding is shown below:[187]

Material	Parts by Weight
Ethylene-Vinyl Acetate	100
HS-200 Silica (filler)	20-100
Methacryloxypropyl Trimethoxy-Silane (Union Carbide Corp.) (coupling agent)	1
Zinc Oxide (lubricant)	2
Zinc Stearate (lubricant)	2
Stearic Acid (lubricant)	1
Trimethylolpropane Trimethyacrylate (coagent) (Sartomer Resins Co.)	1
α-α'-Bis(t-butylperoxy)diisopropyl benzene (Hercules Co.) (crosslinking agent)	3

A typical formulation for a polyvinyl chloride resin-based compound, useful for pipe fittings, is given below:[158]

Material	Parts by Weight
PVC Resin (K60)	100
Internal Lubricant	2.5
Octyl Thiotin Complex (stabilizer)	1.5
Flow Improver	2.5
Filler	0-10

TABLE 77. INJECTION MOLDING INPUT MATERIALS AND PRODUCTS

Polymer	Formulation	Products
Acrylic Resins	Usually requires dessicant drying	Thin wall, complex parts for household, optical, and technical applications
	Antistatics	Automotive lenses
	Colorants	Decorative escutcheons
	Flame Retardants	Nameplates
	Lubricants	Lighting louvers
	UV Stabilizers	Lighting lenses
		Video disk products
		Medallions
		Typewriter buttons and bars
		Pump parts
		Piano keys
ABS	Resin must be dried 2-4 hours at 82-93°C (180-200°F) in a dehumidifying air hopper drier	Appliance housing
		Bobbins and spools
		Boxes, containers, carry cases, tackle boxes
		Flashlight housings
	Antioxidants	Football helmets
	Antistatics	Furniture parts
	Blowing Agents	Household items
	Colorants	Machine housings
	Flame Retardants	Pipe fittings
	Lubricants	Radio cabinets
	Reinforcers	Suitcases
	Stabilizers	Automotive components for instrument panels, consoles, ducts, door post covers, door locks, knobs, radiator grills, and headlight housings
	UV Stabilizers	
		Toys
		Sporting goods
		Hobby kits
		Canoe parts
Fluoroplastics		
PTFE (Teflon®)	Pelletized Resins	Pump components
		Process equipment parts
	Fillers	Tower packings

(continued)

TABLE 77 (continued)

Polymer	Formulation	Products
FEP (Tefzel®)	Pelletized Resins Reinforcers	Process equipment parts Electrical insulators Valve fittings Pumps for corrosive fluids Bearing seals and rings
PVDF (Kynar®)	Pelletized Resins Activators Blowing Agents Colorants Crosslinking Agents Curing Agents Fillers Plasticizers Processing Aids Reinforcers	Valves Pumps Impellers Seals Gaskets Electrical connectors
Nylon 6 and Nylon 6/6	Polymer must be dried 4 to 10 hours at 110°C (230°F) Antioxidants Antistatics Blowing Agents Colorants Fillers Lubricants Nucleating Agents Plasticizers Reinforcers UV Stabilizers	Medical items Precision moldings Shoe heels Military items Cases Cookware Valve caps Automotive parts for fuel vapor recovery, canisters, emissions control components, fan blades, distributor parts, cable ties, dome light covers, and speedometer gears Electrical components for connectors, housings, battery boxes, small motor casings, relay covers, wire ties, switch housings, fuse holders, terminal boxes, grommets, and clips Machine parts for small gasoline engine parts, starter gears, air silencers, carburetors, cams, roller bearings, small gears, sprockets, pulleys, bushings, bearings, and impellers Fasteners Drapery hardware Plumbing hardware

(continued)

TABLE 77 (continued)

Polymer	Formulation	Products
Nylon 6 and Nylon 6/6 (Continued)		Furniture Fixtures Door hardware Tool parts Shower heads Irrigation devices Suspension mechanism for file cabinets Valves for aerosol cans Marine deck fittings Golf club parts Gun stocks Cigarette lighter bodies Spatulas Brush backs Combs Eye glass frames
Phenolics	Colorants Fillers Lubricants Reinforcement	Bearings
Polyacetal	Antioxidants Colorants Reinforcers UV Stabilizers	Conveyors Gears Office supplies Ballcocks Shower heads and faucets Bearings Pushbuttons for telephones Pens Tape cartridges Toys Zippers Aerosol valves Turn signals for autos Specialty electrical parts Molds
Polycarbonate	Resin must be dried 2-4 hours at 127°C (260°F) in a dehumidifying hopper drier Antioxidants Blowing Agents	Automotive parts Battery cases Electrical parts Household items Petri dishes Printed circuit boards Safety shields

(continued)

TABLE 77 (continued)

Polymer	Formulation	Products
Polycarbonate (Continued)	Colorants Flame Retardants Lubricants Mold Release Agents Reinforcers UV Stabilizers	Templates and slide rules Lenses
Polyester		
PBT	Resin must be dried 2-4 hours at 121°C (250°F) Reinforcers	Electrical parts Automotive parts Housewares
PET	Crystalline resin must be dried 2-4 hours at 150-180°C (302-350°F) Antioxidants Antistatics Colorants Flame Retardants Reinforcers	Containers
Polyethylene		
LDPE	Antiblocking Agent Antioxidants Antistatic Agents Blowing Agents Colorants Fillers Flame Retardants Impact Modifiers Reinforcers UV Stabilizers	Bobbins Containers Packaging Lids for coffee cans, margarine tubs, shortening, nuts, and pipe tobacco Toys Novelties Housewares
HDPE	Antiblocking Agents Antioxidants Antistatic Agents Blowing Agents Colorants Flame Retardants Impact Modifiers	Closures and caps Crates, cases, containers and pallets Dairy tubs Housewares Industrial pails, containers and moldings

(continued)

TABLE 77 (continued)

Polymer	Formulation	Products
HDPE (Continued)	Reinforcers Stabilizers UV Stabilizers	Ice cream containers Pails Paint cans Seating components Tote boxes Toys Catsup and mustard containers Ice cube trays Canisters Butter dishes Hard hats Furniture
UHMWPE	Antioxidants Antistatics Colorants Corrosion Inhibitors Crosslinking Agents Fillers Flame Retardants Mold Release Agents Reinforcers Thermal Conductors	Plates and sheets Blocks Rods and tubes
Polyphenylene Oxide		TV parts Filter stacks Filter discs Valve seats Surgical instruments Food trays Small appliance housings Dashboard electrical connectors Knobs and handles Cases Pumps Shower heads
Polyphenylene Sulfide	Colorants Mineral Fillers Reinforcers	Bearings and cams Electronic parts Hair dryer parts Small cooking appliances Range components Valves

(continued)

TABLE 77 (continued)

Polymer	Formulation	Products
Polypropylene	Antiblocking Agents Antioxidants Antistatics Blowing Agents Colorants Fillers Flame Retardants Lubricants Plasticizers Reinforcers Stabilizers UV Stabilizers	Battery cases Closures, lids, caps, and containers Luggage and carry cases Packaging Tables Toys and novelties Washing machine agitators Clothes drier filter housings Dishwasher pump components, silverware baskets, detergent dispensers, inlets and drains Refrigerator ice maker components Room air conditioner air deflectors, condensate pans, filter frames and impellers Television set parts Butter dishes Light shield Ice cube trays Tupperware® Seats Furniture frames Sports equipment Syringes Labware Medical tubing and connectors Automotive door panels, fender aprons, glove compartments, interior trim
Polystyrene	Antioxidants Antistatics Blowing Agents Colorants Fillers Flame Retardants Lubricants UV Stabilizers	Appliance parts Cups, lids, dishes, and cutlery Containers, boxes, vials, jars, and tubs Housewares Refrigerator trays and covers Toys and hobby kits Produce trays Cocktail glasses Sporting goods Soap dishes Handles for kitchen utensils Salt and pepper shakers Coffee servers Watering cans

(continued)

TABLE 77 (continued)

Polymer	Formulation	Products
Polystyrene (Continued)		Room dividers Picture frames Letter trays Calender bases Toilet seats Architectural trim moldings Calculators Tape reels, reel covers, and cassettes Furniture Combs
PVC	Antiblocking Agents Antioxidants Antistatic Agents Blowing Agents Colorants Fillers Flame Retardants Fungicides Impact Modifiers Lubricants Plasticizers Heat Stabilizers UV Stabilizers	Boots Building and construction supplies Bumper parts Business machines and appliance parts Footwear, sandals, heels, and soles Hospital and health care supplies Pipe fittings Plugs and connectors Refrigerator gaskets Toys Filler strips Rear view mirror housings Window winder knobs Bicycle grips
SAN	Resin must be dried for a minimum of 2 hours at 71-82°C (160-180°F) Fillers Lubricants Reinforcers	Appliance parts Automotive parts Cosmetic containers Tumblers Automotive instrument lenses Blender jars and covers Dishes and trays in appliances Medical instruments and utensils Tape reels Picnic ware

(continued)

TABLE 77 (continued)

Polymer	Formulation	Products
Vinylidene Chloride	Antioxidants Heat Stabilizers UV Stabilizers	Gasoline filters Valves Pipe fittings Containers Chemical process equipment parts

Sources: Agranoff, J. (ed). Modern Plastics Encyclopedia 1981-1982, pp. 4, 5, 8, 10, 24, 29, 32, 46, 58, 60, 64, 78, 80, 89, 90, 100, 112.

Bikales, Norbert M. (ed). Encyclopedia of Polymer Science and Technology, (Vol:pp): 6:334; 10:105-109; 13:397-398; 1:431.

Brown, R., Design and Manufacture of Plastic Parts, 1980, p. 84.

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Gaylord, Norman G. (ed). Encyclopedia of Polymer Science and Technology, Vol. 1, p. 431.

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Standen, Anthony (ed). Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edtion, (Vol:pp): 19:109-112; 21:270-274, 295-299.

Webber, Thomas G., Coloring of Plastics, 1979, pp. 81, 92, 96, 97, 104, 109, 110, 139, 141, 169, 172.

A typical formula for a moldable polyester premix is shown below:[219]

Material	Parts by Weight
Polyester Resin	120
Styrene Monomer (dissolve catalyst)	2.4
Calcium Carbonate (filler)	190
Iron Oxide (pigment)	12.0
Aluminum Stearate (lubricant)	2.4
Benzoyl Peroxide (catalyst)	1.2
Fibrous Glass Roving (1/2") (filler)	72

Another typical formulation for a moldable polyester is shown below. This formula can be used to produce synthetic ceramic tile by injection molding.[56]

Material	Parts by Weight
Hexahydrophthalic Rigid Polyester	35
Dimethyl Aniline (mix before adding catalyst)	0.07
t-Butyl Peroctoate (catalyst)	0.4
Pigment	3
Calcium Carbonate (filler)	20
Ground Limestone (filler and colorant)	65
Barytes, No. 1 Bleached (filler)	15

PROCESS DESCRIPTION

The injection molding process begins by feeding the resin and the appropriate additives from the hopper to the heating/injection system of the injection molding machine. The polymer mix is heated to the temperature at which it becomes soft enough to flow. An injection system forces the melt through a nozzle, then through sprues and runners, and finally into the cavities of the mold. High pressure is held briefly to allow the plastic to set. Thermosets require that heat be applied to the mold in order to complete the polymerization. Thermoplastics are cooled in the mold sometimes by the circulation of indirect cooling water. Figures 45 and 46 present diagrams of the injection molding of thermosets and thermoplastics, respectively.

Injection molds are formed from high quality non-porous steel. They are usually vented to allow for the release of trapped air, moisture, and other gases.[155]

The mold halves are mounted on moving and stationary platens which are hydraulically operated. When the part is capable of maintaining the mold shape, the mold halves are opened and the part is ejected either by air pressure or spring loaded ejector pins. The mold then closes to begin a new injection cycle.

Injection molded parts are usually trimmed by automatic trimmers. Sprues, runners, and flash must be removed before the product is ready for further finishing operations such as decorating or labelling. In the case of

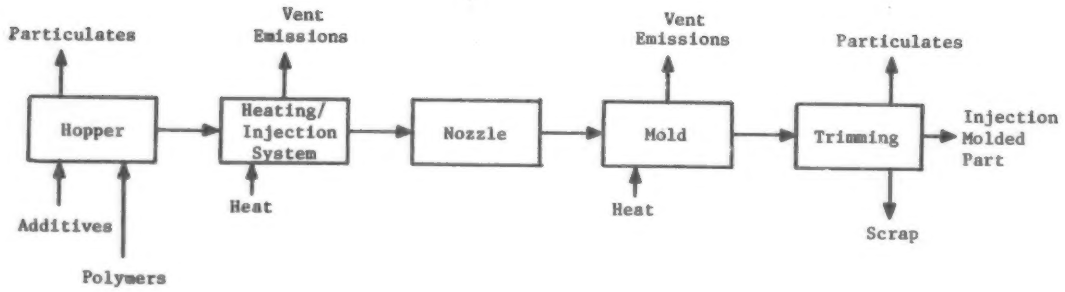
Particulates
Vent Emissions
Vent Emissions
Particulates
Hopper
Heating/ Injection System
Nozzle
Mold
Trimming
Injection Molded Part
Additives
Polymers
Heat
Heat
Scrap

Figure 45. Injection molding of thermosets.

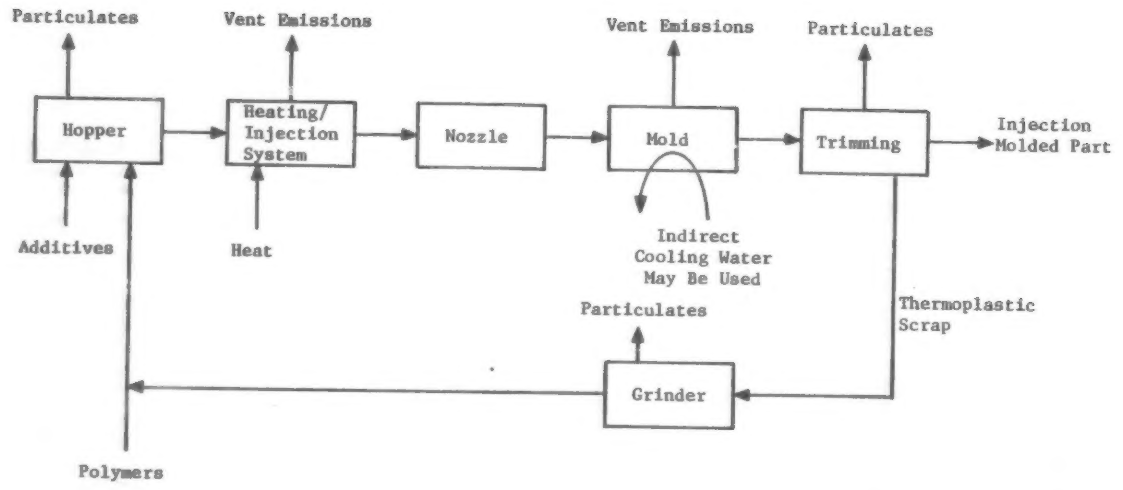
Particulates
Vent Emissions
Vent Emissions
Particulates
Hopper
Heating/
Injection
System
Nozzle
Mold
Trimming
Injection
Molded Part
Additives
Heat
Indirect
Cooling Water
May Be Used
Particulates
Thermoplastic
Scrap
Grinder
Polymers

Figure 46. Injection molding of thermoplastics.

thermoplastics, the scrap and defective parts are ground and recycled to the polymer feed. Thermoset scrap cannot be reused and must be disposed of as a solid waste or may be granulated and used as a filler.

There are four basic types of heating/injection systems used for commercial injection molding. The four types are: (1) conventional injection molding machines, (2) piston-type preplasticating machines, (3) screw type preplasticating machines, and (4) reciprocating-screw injection machines. The reciprocating screw injection machine has become the most common machine for modern plastics processing due to faster cycles, lower melting temperature requirements, and better mixing. A brief description of each of the heating/injection systems follows.

Conventional Injection Molding - The plastic granules or pellets are poured into a machine hopper and fed into the chamber of the heating cylinder. A plunger compresses the material forcing it through progressively hotter zones of the heating cylinder. The material flows from the heating cylinder through a nozzle into the mold. This type of molding machine will produce mottled colored molded parts since colorants are not thoroughly mixed with the plastic material in the heating cylinder unless pre-colored polymers are used as feed.

Piston-Type Preplasticating - This injection molding machine uses a heater to preplasticate the plastic granules. The fluid plastic is then held in a holding chamber until it is molten enough to be forced into the die. A piston then rams the plastic through the nozzle into the mold. This machine produces pieces faster than a conventional machine because the holding chamber can be filled to shot capacity while a part is cooling in the mold. This process is used to produce large molded parts although it is not in wide commercial use.[15]

Screw-Type Preplasticating - In this system, an extruder is used to plasticize the plastic material. The rotating screw feeds the pellets forward to the heated interior surface of the extruder barrel. The molten plastic moves from the extruder into a holding chamber and is forced into the die by an injection plunger. The use of a screw provides:

- better mixing and shear action of the plastic melt,
- better color blending, and
- less stress in the molded part.

Reciprocating-Screw Injection Machine - This type of injection molding utilizes a horizontal extruder in place of the heating chamber. A rotating screw moves the plastic material forward through a heated extruder barrel. As the molten plastic material moves forward, the screw backs up to a limit switch that determines the volume of material collecting in the front of the barrel. The screw then acts as a ram and injects the plastic material into the die. The screw rotates backwards to begin the next cycle. The advantages of this system over the other three are:

- it more efficiently plasticizes heat sensitive materials,
- blends colors more rapidly, and
- heat requirements are lower.

Thermosets are most commonly injection molded in reciprocating-screw injection machines which are similar to those used for thermoplastics. The die temperature is maintained higher than the barrel temperature so that the plastic reaches its cure temperature just as it enters the mold. The mold temperature is maintained at the cure temperature to speed thermoset polymermerization. Once the part has polymerized it is ejected from the mold.

OPERATING PARAMETERS AND UTILITY REQUIREMENTS

The conditions under which injection molding operations are performed are strongly governed by the polymer being processed and the end product application. Most processors use company guidelines to determine rough settings for the temperature, pressure, and screw speed when applicable. The process is then fine-tuned to determine the optimum processing temperature, mold temperature, and injection pressure. Cooling and heating requirements are then determined to maintain the necessary operating parameters.

The injection molding of thermoplastics requires that the polymer be sufficiently plasticized in order to allow it to flow through the nozzle and sprues to the mold cavities. Table 78 presents typical processing temperatures for thermoplastics and thermosets used for injection molding.

The mold temperature for thermoplastic processing must be maintained below the softening point of the material being molded. It must also be high enough to prevent shrinkage of the plastic due to hardening of the outside of the mass too quickly. Mold temperatures for thermoplastics generally range from 52 to 149°C (125 to 300°F).[10]

The injection molding process for thermoset plastic processing requires the mold to be heated to complete crosslinking. The thermoset reaches the processing temperature just as it goes through the injection nozzle. The mold is maintained at the processing temperature until the part has cured sufficiently to hold the desired product shape. Steam or electricity are usually used to maintain the correct mold temperature.

Injection molding machines most commonly use electric heaters to provide the necessary heat input. Several mica insulated heater bands of high wattage are used for each zone of the injection cylinder. Thermocouples and pyrometers are used to maintain the appropriate processing temperature along the molder barrel.[212] Table 79 presents a summary of the heat and power requirements for a range of injection molding machine capacities.

Injection molding cycle times vary according to the design of the product and the polymer formulation being utilized. Typical cycle times generally range from 10 to 35 seconds; however, they can be as short as one second for very small parts and as long as 120 seconds for larger, more intricate parts.[16] The time consuming segment of the injection molding cycle is the in mold time. For thermoplastics, this is the cooling time and for thermosets this is the cure time. Non-contact cooling water within the mold halves is used to speed up the cooling of thermoplastic parts.

TABLE 78. INJECTION MOLDING TEMPERATURES

Polymer	Processing Temperature °C†
Thermoplastics	
Acrylic Resins	180 - 250
ABS	180 - 240
Fluoroplastics	
ETFE	260 - 330
FEP	200 - 260
PVDF	260 - 330
Nylon 6	260 - 290
Nylon 6/6	270 - 300
Polyacetal	185 - 225
Polycarbonate	280 - 310
Polyester	
PBT	232 - 260
PET	270 - 300
Polyethylene	
LDPE	160 - 240
HDPE	200 - 300
EVA	200 - 280
Polyphenylene Oxide	280 - 340
Polyphenylene Sulfide	315 - 330
Polypropylene	200 - 275
Polystyrene	180 - 260

(continued)

TABLE 78 (continued)

Polymer	Processing Temperature °C†
Polyvinyl Chloride	160 - 210
SAN	180 - 240
Thermosets	
Diallyl Phthalate	170 - 180
Melamine Formaldehyde	160 - 170
Unsaturated Polyesters	232 - 260
Urea Formaldehyde	150 - 160

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†For thermoplastics, the processing temperature is the plastic temperature just prior to the injection nozzle. For thermosets, the processing temperature is reached at the injection nozzle and is maintained in the mold.

Sources: Bikales, Norbert M. (ed). Encyclopedia of Polymer Science and Technology, Vol. 10, p. 108.

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S.P.E., "Injection Molding of Plastics," Injection Molding Conference, 1980, p. 77.

Weir, C. L., Introduction to Injection Molding, 1975, p. 19.

TABLE 79. INJECTION MOLDING HEAT AND POWER INPUT REQUIREMENTS

Machine Capacity		Approximate Heat Input	Power Input to Motor	
lbs/hr	kg/hr	kW	hp	kW
17.5	38.5	2 - 2.5	5.5	4.1
45	99	2.8 - 4.1	5	3.7
80	176	4.4 - 5.2	10	7.5
125	275	8.5 - 9.0	15	11.2
220	484	9.0 - 10.5	25	18.6
250	550	10.6 - 12.0	40	29.8
400	880	15 - 20	50	37.3
440	968	20 - 25	60	44.7
700	1540	25 - 30	75	55.9
750	1650	30 - 40	90	67.1
850	1870	40 - 50	100	74.6
1000	2200	60 - 70	125	93.2
1500	3300	68 - 75	150	111.9
1800	3960	75 - 100	200	149.1

Source: Weir, Clifford L., Introduction to Injection Molding, 1975, p. 19.

Injection pressures range from 6.9 to 20.7 x 10^7 Pa (10,000 to 30,000 psi) with most applications requiring pressures between 8.3 to 13.8 x 10^7 Pa (12,000 to 20,000 psi).[81]

WASTE STREAMS AND EMISSIONS

Injection molding operations produce air emissions and solid waste. No wastewater is produced since water is used only in the indirect cooling of the mold halves. Table 80 presents a summary of the point source emissions from injection molding operations. The waste streams and emissions resulting from major plastics additives are detailed in the Industry Description section of this document.

Air Emissions - Injection molding operations have the potential to produce particulate and hydrocarbon emissions. Particulates are produced from the polymer feed and mixing in the hopper. Particulates are also produced by the trimming of the parts and the grinding of thermoplastic sprues, runners, and other scrap. These particulates consist of particles of polymer and additives.

Volatile emissions are liberated from vents in the heating/injection cylinders and the molds. These emissions consist of traces of monomers, additives, and decomposition products. Decomposition products occur when the processing temperature reaches that temperature at which the polymer begins to decompose. Table 81 presents those decomposition products which could be formed during injection molding operations.

Solid Waste - Thermoplastic sprues, runners, and scrap generated by the trimming of product flash can usually be ground and recycled to the hopper feed. Virgin resin and regrind are usually mixed in a 4:1 ratio.[16] Excess scrap and particulates which cannot be recycled must be disposed of as solid waste. Thermoset plastic which remains in the feed channels to the mold cavity and which is trimmed from parts must also be disposed of. Since this waste is comprised of inert plastic material, it will pose no disposal problems.

WORKER DISTRIBUTION AND EXPOSURE

Injection molding operations are relatively automated. Both thermoplastic and thermosetting polymers may be injection molded. Except for a scrap grinding and recycle operation for thermoplastics, employee manpower requirements are similar for processes molding both types of plastics.

Worker distribution estimates shown below have been made by correlating major equipment manhour requirements with the process flow diagrams in Figures 45 and 46.

TABLE 80. INJECTION MOLDING POINT SOURCE EMISSIONS

	Air Emissions					Solid Waste		
	Particulates		Volatiles					
	Polymer	Additives	Monomer	Additives	Decomposition Products	Polymer	Plasticizer	Additives
Hopper	X	X						
Heating/Injection System			X	X	X			
Mold			X	X	X			
Trimmer	X	X				X	X	X
Grinder	X	X						

TABLE 81. DECOMPOSITION PRODUCTS

Polymer	Highest Processing Temperature (°C)†	Decomposition Temperature (°C)§	Decomposition Products
Acrylic Resins	250	320	*
ABS	240	300	*
Diallyl Phthalate	175	285	*
Fluoroplastics	330	300	HF
Melamine Formaldehyde	170	182	*
Nylon 6 and 6/6	290	300	*
Phenolic	205	300	*
Polyacetal	225	250	*
Polybutylene	190	300	*
Polycarbonate	310	330	*
Polyester (Thermoplastic)	300	300	acetaldehyde
Polyester (Thermoset)	260	275	*
LDPE	240	100	Ketone carbonyl groups form due to oxidation
HDPE	300	100	
EVA	280	100	
Polyphenylene Sulfide	330	700	*
Polypropylene	275	300	*
Polystyrene	260	300	*
PVC	210	100	HCl
SAN	240	300	*
Urea Formaldehyde	160	182	*

---

*Decomposition products are not formed at or near injection molding temperatures.

†This is the highest possible temperature reached by the normal injection molding of all formulations of the polymer listed.

§This is the lowest temperature at which decomposition products begin to form.

Unit	Workers/Unit/8-hour Shift
Mixing/Blending	0.5
Molding	0.5
Trimming	0.25
Scrap Grinding (thermoplastics only)	0.25

Because a wide variety of polymers are formed commercially by injection molding, employees potentially may be exposed to numerous particulate and gaseous materials. Actual exposure parameters must be determined for individual plants through implementation of a comprehensive employee monitoring program. However, probable release points and contaminants which may be present in injection molding operations are identified in Table 82. Toxicity information for these contaminants is given in Appendix C of this document and IPPEU Chapters 10 and 10b.

TABLE 82. INJECTION MOLDING EMISSIONS AND RELEASE POINT ESTIMATION

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent	
Hopper	Fugitives	[1]Polymer Particulates	
		[2]Additive Particulates:	Antioxidants - BHT - trisnonyl phenyl phosphite - dilauryl thiodipropionate
			Colorants - carbon black - titanium dioxide - Cd sulfoselenide - lead chromate - phthalocyanines - anthraquinone red - monoazo yellow
			Flame Retardants - antimony oxide - alumina trihydrate - trixylenyl phosphate - decabromodiphenyl oxide - chlorinated paraffin wax
			Heat Stabilizers - tribasic lead sulfate - Ba/Cd stearate - Ca/Zn stearate

(continued)

TABLE 82 (continued)

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Hopper (continued)		UV Stabilizers - 2-hydroxy-4-octoxy benzophenone - 2 (2'-hydroxy-5'-methyl) phenyl benzotriazole) - nickel dibutyldithio carbonate
		Plasticizers - dioctyl phthalate - diisooctyl phthalate - diisodecyl phthalate - di (2-ethylhexyl) phthalate - tricresyl phosphate
		Reinforcers - glass fibers - asbestos - silica
		Noise

(continued)

TABLE 82 (continued)

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Heating/Injection System	Heater Vent Fugitives	[3]Volatile Monomer - methyl methacrylate - acrylonitrile - 1,3 butadiene - styrene - 2,6-xylenol - p-dichlorobenzene - fluorocarbons - phenol - formaldehyde - caprolactam - hexamethylenediamine - 1-butene - vinyl chloride - bisphenol-A - ethylene glycol - dimethylterephthalate - terephthalic acid - 1,4-butanediol - ethylene - propylene - 1-butene - 1-hexene - 1-octene - vinylidene chloride
		[2]Volatile Additives
		Decomposition Products - HF (fluoropolymers) - acetaldehyde (polyethylene terephthalate) - ketone carbonyls (polyethylenes) - HCl (polyvinyl chloride)

(continued)

TABLE 82 (continued)

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Molding	Mold Vents Fugitives	[3]Volatile Monomer
		[2]Volatile Additives
		Decomposition Products
Trimming and Grinding	Fugitives	[1]Polymer Particulates
		[2]Additive Particulates
	Trimming Tools	Noise

---

[1] See list on pages 264-271.

[2] Major additives documented in the literature. Other additives may be present, depending on product specification.

[3] Principal monomers used to produce the polymers typically formed through injection molding. Other monomers or comonomers may be present.

SECTION 16

REACTION (LIQUID) INJECTION MOLDING

FUNCTION

Reaction injection molding (RIM) is a relatively new process that is rapidly taking its place alongside the more established processing operations. RIM is predicted to be one of the more rapidly growing sectors of the plastics processing industry in the future.

RIM involves the simultaneous high pressure injection of two or more reactive liquid streams into a mixing chamber, followed by low pressure injection into a mold cavity where the polymerization is completed. The advantages of reaction injection molding over injection molding lie in reduced mold costs, lower equipment costs, and lower temperatures, pressures, and energy requirements.

INPUT MATERIALS AND END PRODUCTS

All commercial reaction injection molding to date has been performed with various urethane formulations. RIM systems utilizing epoxies, polyesters, polyamides, and nylon 6 are currently under development. Systems utilizing reinforced nylon are approaching commercialization for use in the automobile industry.

Urethane systems have traditionally been used for RIM because they readily meet processing and performance requirements. The RIM process requires liquid intermediates which can be catalyzed to provide rapid polymerization at low temperatures without producing gaseous by-products.[119] Most urethane systems are comprised of two liquid intermediate feeds: the resin and isocyanate. Chain extenders and the catalyst are added to the resin feed. When blowing agents are incorporated in the isocyanate feed, foam products are formed. The production of such foam products is discussed in the Foaming section of this document.

Reaction injection molded polyurethane products are utilized in the automotive and recreation industries. New applications for RIM parts are continually being found. Table 83 presents typical formulations and products of reaction injection molding. Reinforced reaction injection molding has developed rapidly over the past few years to provide more durable products which undergo less thermal expansion. The production of such products is discussed in the Reinforced Plastics section while more information on major plastics additives used in RIM is presented in the Industry Description section of this document.

TABLE 83. TYPICAL REACTION INJECTION MOLDING PRODUCTS

Urethane Type	Characteristics	Products	Formulations Include
Low-modulus elastomers	Tough Resilient	Bumper system fascias Panelling	Antioxidants Blowing Agents Colorants Flame Retardants Flow Controllers Fillers Modifiers Lubricants Plasticizers Reinforcing Agents Surfactants Urethane Catalysts UV Stabilizers
High-modulus elastomers	Rigid	Automotive trim Agricultural equipment Business machines Furniture Machinery housing Radio and TV cabinets Recreational vehicle components Sporting goods Skis Shoe soles Solar collectors	

Sources: Becker, Walter E., Reaction Injection Molding, 1979, pp. 22, 44, 50.

Frados, Joel, Plastics Engineering Handbook of the Society of the Plastics Industry, Inc., 1976, p. 512.

Webber, Thomas G., Coloring of Plastics, 1979, pp. 198-203.

A typical RIM polyol system has the following formulation:[16]

Material	Parts by Weight
Polyether Polyol (MW = 3,000-6,000; tipped with ethylene oxide)	75 - 80
1,4-Butanediol (chain extender)	17 - 20
Triethylene Diamine (catalyst)	0.6 - 1.0
Dibutyltin Dilaurate (catalyst)	0.01 - 0.05
Water	0.1 - 0.2
$CFCl_3$ and/or CH_2Cl_2 (blowing agent)	2 - 6
Modified MDI Isocyanate (e.g., Mondur PF or Mondur CD) (reactant)	Index 101 - 103

PROCESS DESCRIPTION

As shown in Figure 47, the reaction injection molding process is comprised of five integrally related units: feed tank, metering, mixing, molding and trimming. The first of these units includes the feed tanks in which the raw material components are stored and heated. Agitator, heat exchangers, low-pressure pumps, and recirculation equipment are utilized to maintain liquid temperature and uniformity. Liquid streams from the feed tanks are metered by either high-capacity metering pumps or piston displacement to the mixing head. The mixing head is mounted on the mold and contains a cylindrical mixing chamber where the liquid streams are mixed under high-pressure. The well mixed liquid streams are immediately injected into the mold where polymerization begins. RIM molds are equipped with a runner and a gate which is designed to insure laminar flow into the mold cavity, since turbulent flow entrains unwanted air bubbles.

The mold acts as a chemical reactor where the polyurethane polymer is formed. Heat addition to the mold is not required due to the exothermic nature of the polyurethane cure reaction. Indirect cooling of the mold may be required to control the cure temperature. High volume production molds are generally constructed from machined or cast steel. Once the part has sufficiently cured to hold its shape, the mold is opened and the part is ejected. The mold is sprayed with a release agent before closing in preparation for the next shot.

Reaction injection molded parts are trimmed of flash before they are sent to finishing operations. Polyurethane scrap cannot be recycled.

OPERATING PARAMETERS AND UTILITY REQUIREMENTS

Actual operating parameters for reaction injection molding must be determined specifically for each product and polymer formulation. The temperatures of the unreacted liquid feed streams leaving the storage tanks are in the range of 24 to 66°C (75 to 150°F).[119] Mold temperatures typically range from 49° to 77°C (120 to 170°F) due to the exothermic nature of the reaction.[119]

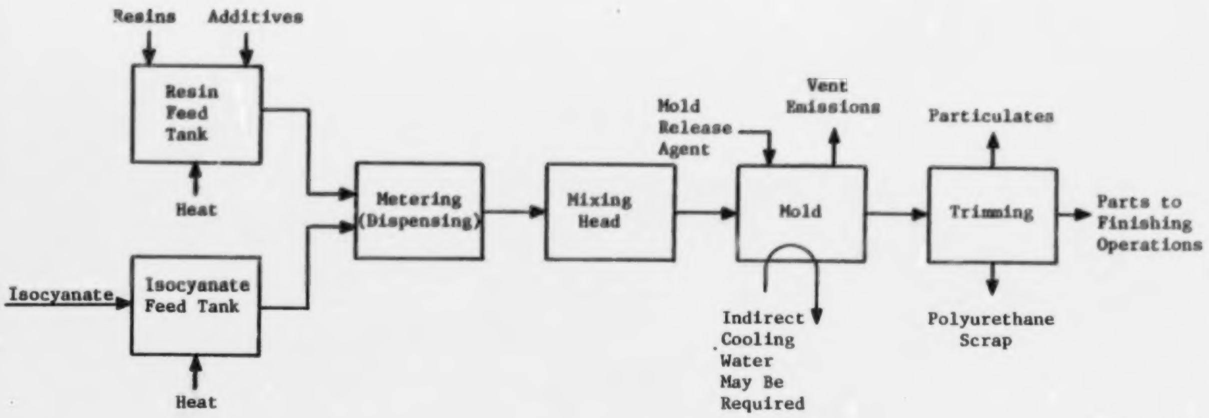
Resins
Additives
Resin Feed Tank
Heat
Isocyanate
Isocyanate Feed Tank
Heat
Metering (Dispensing)
Mixing Head
Mold Release Agent
Vent Emissions
Mold
Indirect Cooling Water May Be Required
Particulates
Trimming
Polyurethane Scrap
Parts to Finishing Operations

Figure 47. Reaction injection molding.

Typical RIM cycle times range from 1.5 to 4 minutes. A breakdown of the cycle time for polyurethane elastomers is shown below:[38]

Operation	Time (Seconds)
Injection	2 - 5
Polymerization	18 - 55
Mold Opening/Part Removal	20 - 60
Cleaning/Inspection	30 - 60
Mold Release Spraying/Closing	30 - 60
TOTAL CYCLE	100 - 240

Feed streams are pumped at about 1.7×10^7 Pa (2,500 psi) through the nozzle into the mixing head. In-mold pressures are normally less than 3.4×10^5 Pa (50 psi) and therefore, RIM processing requires less clamping force than many other processes.[119]

Due to the low temperatures and pressures used in RIM processing, only 10 to 30 percent of the energy needed for injection molding is required.[119]

WASTE STREAMS AND EMISSIONS

Reaction injection molding operations produce air emissions and solid waste. No wastewater is produced since water is not used during the process. Table 84 presents a summary of the point source emissions from RIM operations. Emissions and wastes are discussed in more detail in the text below. Major plastics additives used in RIM are discussed in more detail in the Industry Description section of this document.

Air Emissions - Reaction injection molding produces volatile and particulate emissions. Particulate emissions are generated by the trimming of product flash. Such particulates consist of fine particles of polymer and additives. Since the feed to reaction injection molding is in the liquid form, particulates are typically not generated during the mixing or dispensing of the feed.

Reaction injection molding may also produce volatile emissions. Generally a vent is incorporated in the mold design at the highest point in the mold. For highly intricate parts, venting may be done by means of vent pins or drag plates.[16] Urethane systems may be utilized which do not produce gaseous by-products. Decomposition products are not formed since in-mold temperatures do not exceed the 300°C lower limit for the decomposition of polyurethane. The presence of humidity at the processing temperature may cause hydrolysis of the urethane functional groups; however, humidity in the feed streams is generally carefully controlled.

Solid Waste - Polyurethane scrap is produced by the trimming of reaction injection molded products. Polyurethane scrap cannot be recycled to the process feed since the feed is comprised of liquid intermediates which are crosslinked and completely polymerized during the molding process. Scrap from trimming operations is comprised of polyurethane which has been polymerized

TABLE 84. REACTION INJECTION MOLDING POINT SOURCE EMISSIONS

	Air Emissions					Solid Waste	
	Particulates		Volatiles				
	Polymer	Additives	Monomers	Cure Reactor	By-Products	Polymer	Additives
Mixing			X		X		
Molding			X	X	X		
Trimming	X	X				X	X

and crosslinked and therefore cannot be recycled to the feed. No problems should be presented by the disposal of such waste due to the characteristic inertness of the polymer.

WORKER DISTRIBUTION AND EXPOSURE

Like previously-discussed molding operations, RIM operations are highly automated. Estimated worker distribution, based on equipment manpower requirements is shown below:

Unit	Workers/Unit/8-hour Shift
Storage	0.5
Heat Exchanger	0.125
Molding	0.5
Trimming	0.5

Automation of RIM operations effectively reduces employee exposure potential to the isocyanate component used in the process. However, fugitive emissions or process upset conditions may result in employee exposure to volatile isocyanates and additives. Trimming operations may produce exposure to polymer and additive particulates.

Probable release points and contaminants generated in RIM operations are shown in Table 85. Toxicity information regarding the contaminants in Table 85 is found in Appendix C and IPPEU Chapters 10 and 10b.

TABLE 85. REACTION INJECTION MOLDING EMISSIONS AND RELEASE POINT ESTIMATION

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Storage/Mixing	Fugitives	Volatile Monomer - polyether polyols
		[1]Volatile By-Products
		[2]Volatile Isocyanates
Molding	Mold Vents Fugitives	Volatile Monomer
		[1]Volatile By-Products
		[2]Volatile Isocyanates
Trimming	Fugitives	Polymer Particulates - urethane
		[3]Additive Particulates: Colorants - carbon black - titanium dioxide - Cd sulfoselenide - lead chromate - phthalocyanines Urethane Catalysts - triethylene diamine Plasticizers - dioctyl phthalate - diisooctyl phthalate Reinforcers - glass fibers - silica
	Trimming Tools	Noise

[1] Unspecified.
[2] Toluene-2,4-diisocyanate, methylene bisphenyl isocyanate, methylene bis (4-cyclo-hexylisocyanate).
[3] Major additives documented in the literature. Many other additives may be present, depending on product formulation specifications.

SECTION 17

ROTATIONAL MOLDING

FUNCTION

Rotational molding, sometimes termed rotomolding or rotocasting, is used to make rigid or flexible thin-walled hollow objects from thermoplastic materials. This molding process is capable of producing irregular hollow objects of all sizes and is especially suitable for the production of medium to large items. Unlike blow molding, rotational molding can produce parts with very little stress since cooling rates are slow enough to relieve stresses. Multi-layer and double wall parts can also be easily produced by rotational molding.

Rotational molding involves placing polymer powder or liquid into a heated hollow mold. The mold is rotated to allow the polymer to coat the inner mold surface. The mold is cooled and the part is ejected.

INPUT MATERIALS AND END PRODUCTS

Rotational molding is performed almost exclusively with thermoplastic resins although small volumes of thermoset resins are utilized in research products and specialty parts.

Major resin feedstocks to rotational molding include:

- Polyamide Resins (Nylons)
- Polyacetal
- Polycarbonate
- Polyester
- Low Density Polyethylene (LDPE)
- Polypropylene
- Polyvinyl chloride (PVC)

Applications for crosslinkable high density polyethylene (HDPE) and linear low density polyethylene (LLDPE) are currently under development. Resin feeds are primarily fine powders (typically in the range of 26 to 60 mesh) [190] with the actual particle size determined by the material flow properties and the contours of the part being produced. The exception to this is PVC which is usually utilized for rotational molding as a liquid plastisol. PVC plastisols consist of fine resin particles and additives dispersed in plasticizers and they are used extensively in the toy and novelty industry. Plastisols can be formulated in a wide range of viscosities, physical characteristics, and colors. Recent modifications have included the addition of acrylic monomers to PVC plastisols thereby producing parts which are very rigid.[65] Other PVC plastisol additives may include antioxidants, antistatics, brightners, colorants, fillers, flame retardants, fungicides, heat stabilizers, and UV stabilizers. Other rotational molded plastics incorporate additives typical for the polymer. More detailed information on major plastics additives used in rotational molding is presented in the Industry Description section of this document.

Typical formulations useful for rotational molding of PVC-based resins are presented below:[158]

Material	Parts by Weight	Useful For
Corvic P65/54 (resin)	100	Doll parts or footballs
Dialkyl 79 Phthalate (plasticizer)	40	
Di-Nonyl Phthalate (plasticizer)	50	
Liquid Calcium/Barium (stabilizer)	3	
Corvic P65/54 (resin)	50	Harder objects
Corvic D55/3 (resin)	50	
Pliabrac 810	25	
Lubrol MOA (lubricant)	2	
Liquid Cadmium/Barium (stabilizer)	3	
P65/54A (resin)	70	Arm-rest skins
D55/3 (resin)	30	
Di-Nonyl Phthalate (plasticizer)	50	
Resmol MN	10	
Paraplex G62 (epoxy stabilizer)	2	
Ferroclere 1776 (stabilizer)	2	
Lubrol MOA (lubricant)	2	

The rotational molding process is used to produce a wide range of industrial and consumer goods. Table 86 presents a list of typical rotational molded products.

PROCESS DESCRIPTION

Rotational molding is a relatively simple process. High production rates can be achieved during rotational molding by passing the mold through a number of process stations. As shown in Figure 48, molds rotate from the loading to heating to cooling to ejection stations.

Prior to being loaded into the mold, the resins and additives are formulated and blended. For a more detailed discussion of blending processes, see the Compounding section of this document. Particulates are released during the polymer blending. Premeasured charges of the polymer powder or liquid are put into the preheated mold at the mold loading station. The polymer containing mold is then put in the circulating hot air oven where it is simultaneously rotated through 360° around two perpendicular axes. Some specific applications require rotations of less than 360° on one axis. This is accomplished by rocking or tilting the mold until even polymer distribution is obtained.[10] The heat forces the thermoplastic to melt and the rotation uniformly distributes the polymer over the entire mold surface. The polymer gel takes the shape of the desired hollow part.

TABLE 86. ROTATIONAL MOLDED PRODUCTS

Apparel display forms
Artificial fruits
Automotive arm rests
Chemical tanks
Decorative bottles
Doll parts
Duck decoys
Flower pots
Food storage bins
Footballs
Fuel tanks
Golf carts
Helmets and other sporting equipment
Hobby horses
Ice chests
Large commercial and industrial containers
Lawn ornaments
Light globes
Squeeze toys
Swimming pool safety floats
Syringe bulbs
Tanks for water and wastes
Traffic cone markers
Trash cans

Sources: Baird, R. J., *Industrial Plastics*, 1971, p. 101.

Fair, R. L., "Rotational Molding," *Modern Plastics Encyclopedia 1981-1982*, p. 400.

Milby, R. V., *Plastics Technology*, 1973, p. 439.

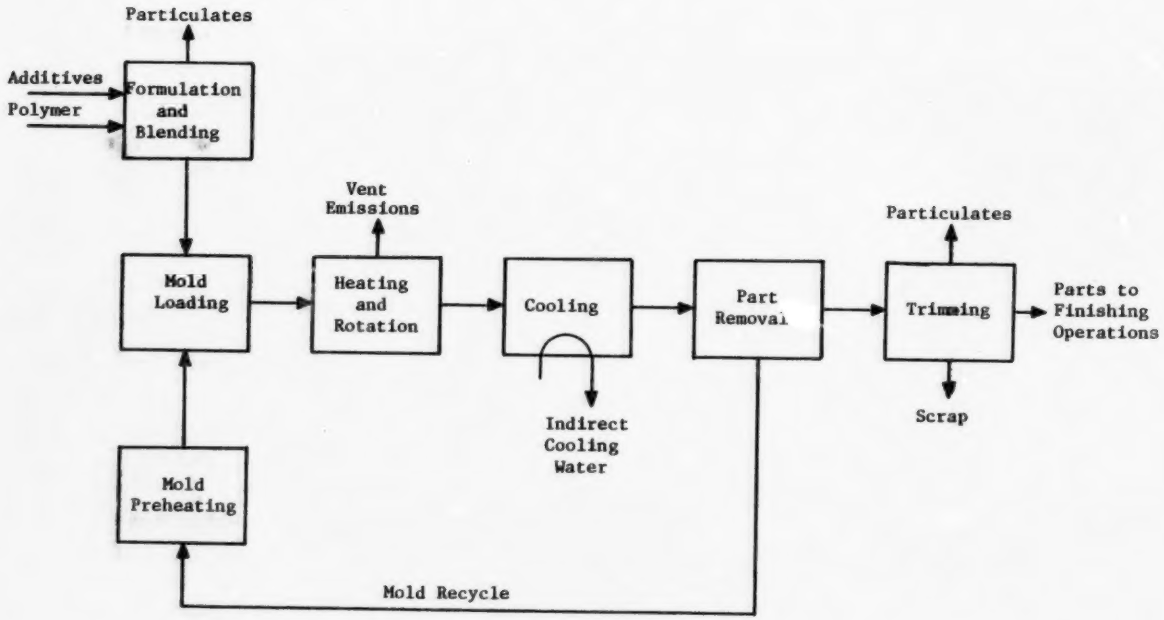
Particulates
Additives
Polymer
Formulation and Blending
Vent Emissions
Mold Loading
Heating and Rotation
Cooling
Part Removal
Particulates
Trimming
Parts to Finishing Operations
Indirect Cooling Water
Scrap
Mold Preheating
Mold Recycle

Figure 48. Rotational molding.

The mold is then removed from the heating oven and is cooled, usually by direct water sprays, at the cooling station. Applications are being researched to speed cooling by blowing nitrogen, carbon dioxide, or compressed air into the mold cavity.[59] After the part has cooled sufficiently to hold the desired shape, the mold is opened and the part is usually removed manually. Trimming operations remove mold parting line flash, and the parts go on to finishing operations such as painting or labeling.

Rotational molds are usually made of cast or sheet aluminum or plated nickel, which is highly polished and has a well-sealed parting line. Small parts are molded in multiple cavity molds, whereas individual molds are generally used for larger parts. Asbestos board or silicone foam can be applied to areas of the mold where polymer adhesion is not desired, as in the case of container openings. The rotomolding process can produce detailed finishes on the mold side of the product. Textured, matted, or highly glossed finishes can be obtained.

OPERATING PARAMETERS AND UTILITY REQUIREMENTS

The temperature used during the heating cycle of rotational molding ranges from 260 to 480°C (500 to 586°F).[15] The exact temperature is determined during trial runs and is dependent upon the size and shape of the part as well as the polymer formulation.

Rotational molding is performed at ambient pressure. Typical molding cycles range from 2 to 17 minutes per part.[65]

WASTE STREAMS AND EMISSIONS

Rotational molding operations have the potential to produce air emissions and solid waste. No wastewater is produced since water is used only in the indirect cooling of the mold. Table 87 presents a summary of the point source emissions from rotational molding operations. More detailed information on waste streams and emissions from major plastics additives used in rotational molding is presented in the Industry Description section of this document.

Air Emissions - Rotational molding operations have the potential to produce particulate and hydrocarbon emissions. Particulates are produced during formulation and blending of powder polymers prior to mold loading. Particulates are also produced by the trimming of rotational molded product flash. These particulates consist of fine particles of polymer, plasticizer, and additives.

Volatile emissions are liberated from the heating and rotation station. These emissions consist of traces of monomers, plasticizer, and decomposition products. Decomposition products occur when the processing temperature reaches that temperature at which the polymer begins to decompose. Table 88 presents those decomposition products which could be formed during rotational molding operations.

Solid Waste - Thermoplastic scrap generated by the trimming of rotational molded product flash cannot be reused for rotomolding operations due to the

TABLE 87. ROTATIONAL MOLDING POINT SOURCE EMISSIONS

	Air Emissions					Solid Waste		
	Particulates		Volatiles					
	Polymer	Additives	Monomer	Additives	Decomposition Products	Polymer	Plasticizers	Additives
Formulation/Blending	X	X						
Heating			X	X	X			
Trimming	X	X				X	X	X

TABLE 88. DECOMPOSITION PRODUCTS

Polymer	Highest Processing Temperature (°C)†	Decomposition Temperature (°C)§	Decomposition Products
Nylons	480	300	CO_2, CO, NH_3, H_2O
Polyacetal	220	250	*
Polycarbonate	300	330	*
LDPE	480	100	Ketone carbonyl groups form due to oxidation
PVC	480	100	HCl

---

*Decomposition products are not formed at or near rotational molding temperatures.

†This is the highest possible temperature reached by the normal rotational molding of all formulations of the polymer listed. Processing temperature ranges were found in the reference literature for polyacetal and polycarbonate. Generally, rotational molding temperatures range from 260 to 480°C.[15]

§This is the lowest temperature at which decomposition products begin to form.

quality of feed required for rotomolding operations. It is sometimes ground for reuse in other processing operations. Scrap should pose no disposal problems since it is comprised of primarily inert plastic material.

WORKER DISTRIBUTION AND EXPOSURE

Manpower requirements for rotational molding operations are similar to those for RIM, except that parts typically are manually removed from rotational molds. Worker distribution estimated by correlating equipment manhour requirements with the process flow diagram in Figure 48, is shown below:

Unit	Workers/Unit/8-hour Shift
Formulation/Blending	0.5
Molding	0.5
Heat Exchanger	0.125
Part Ejection	0.25
Trimming	0.25

Table 89 identifies probable release points and contaminants which potentially result from rotational molding operations. Toxicity information for these contaminants is summarized in Appendix C of this document and discussed in IPPEU Chapters 10 and 10b.

TABLE 89. ROTATIONAL MOLDING EMISSIONS AND RELEASE POINT ESTIMATION

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Formulation/Blending	Fugitives	[1]Polymer Particulates - polyamides
		- polyacetals
		- polycarbonates
		- PBT/PET
		- LDPE
		- polypropylene
		- polyvinyl chloride
		[2]Additive Particulates: Antioxidants - BHT
		- trisnonylphenyl phosphite
		- dilauryl thiodipropionate
		Colorants - carbon black
		- titanium dioxide
		- Cd sulfoselenide
		- phthalocyanines
		Flame Retardants - antimony oxide
		- decabromodiphenyl oxide
		- chlorinated paraffin wax
		Heat Stabilizers - Ba/Cd stearate

(continued)

TABLE 89 (continued)

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Formulation/Blending (continued)		**Plasticizers** - dioctyl phthalate - diisooctyl phthalate - diisodecyl phthalate - tricresyl phosphate - di- (2-ethylhexyl) phthalate
	Mixing Machines	Noise
Heating	Heating Oven Vent Fugitives	[3]Volatile Monomer - formaldehyde - ethylene oxide - caprolactam - hexamethylenediamine - bisphenol-A - ethylene glycol - terephthalic acid - dimethyl terephthalate - 1,4-butanediol - ethylene - 1-butene - 1-hexene - vinyl chloride

(continued)

TABLE 89 (continued)

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Heating (continued)		- 1-octene - vinyl acetate - propylene
		[2]Volatile additives
		Decomposition Products - CO, CO_2, NH_3 (polyamides) - ketone carbonyls (polyethylenes) - HCl-polyvinyl chloride
Part Ejection	Fugitives	[3]Volatile Monomer
		[2]Volatile Additives
		Decomposition Products
Trimming	Fugitives	[1]Polymer Particulates
		[2]Additive Particulates
	Trimming Tools	Noise

[1] Polymers typically formed via rotational molding. Other polymers may be formed in this way for specialty applications.

[2] Major additives cited in the literature. Many other additives may be used, depending on product formulation specifications.

[3] Principal monomers used to produce the plastics typically formed via rotational molding. Other monomers or comonomers also may be present.

SECTION 18

TRANSFER MOLDING

FUNCTION

Transfer molding is one of the most commonly used methods of producing solid molded objects from thermosetting resins. The molding process is much like compression molding with the difference being that in transfer molding the resin is preheated in a chamber separate from the mold and is forced into the mold cavity for curing.

Transfer molding differs from compression molding in that it:

- is economically more attractive for some product applications since it can be highly automated thereby reducing the cycle times;
- injects the plastic material into closed molds thereby minimizing parting line flash;
- provides more uniform cures; and
- can produce intricate parts with or without delicate inserts.

INPUT MATERIALS AND END PRODUCTS

The thermoset resins formulations used for transfer molding are similar to those used in compression molding (see Section 14 for typical formulations for compression molding). Resins utilized for transfer molding are available from the producer in fine powders, granules, and flakes. Commonly used formulations are also available as premeasured preforms, tablets, or slugs of polymer. The majority of polymers which are transfer molded are thermoset resins. Smaller volumes of thermoplastics are transfer molded for special applications. Polymers which are most commonly transfer molded include:

- Alkyd Resins
- Amino Resins
  - Melamine Formaldehyde
  - Urea Formaldehyde
- Diallyl Phthalate (DAP)
- Epoxy Resins
- Phenolic Resins
- Polyester Resins
- Polyimide

Fillers are often used during transfer molding to give the finished product the desired properties and strength. Fillers and other additives used with commonly transfer molded thermosets are shown in Table 90. More detailed information on major plastics additives used in Transfer Molding is presented in the Industry Description section of this document.

TABLE 90. COMMONLY USED TRANSFER MOLDED FILLERS AND OTHER ADDITIVES

		Alkyd Resins	Diallyl Phthalate	Epoxy	Melamine	Phenolic Resins	Polyester	Urea Formaldehyde
Fillers	Antimony Oxide	X	X					
	Asbestos	X	X	X	X	X	X	
	Cellulose		X		X	X	X	X
	Clay	X	X				X	
	Glass Fibers	X	X	X	X	X	X	
	Macerated Fabric				X	X		
	Metals			X				
	Minerals	X	X	X	X	X	X	
	Silica		X	X				
	Synthetic Fabrics	X	X				X	
Other Additives	Catalysts	X			X			X
	Colorants	X			X	X		X
	Crosslinking Agents		X					
	Curing Agents		X	X				
	Flame Retardants	X						
	Flow Improvers	X				X		
	Inhibitors		X					
	Lubricants			X	X			X
	Promoters		X					
	Reodorants	X				X		
	Stabilizers				X			X

Transfer molding is especially well suited for the production of small intricate thermoset parts which would be difficult to compression mold. One of the biggest uses of transfer molding is in the production of electrical insulating parts and connectors (some smaller than a paper clip). Parts which have delicate inserts made of brass, steel, aluminum, copper, plastic, or silver or gold plate are also produced by transfer molding. Table 91 lists some typical products produced by transfer molding.

PROCESS DESCRIPTION

Input materials for transfer molding include resin, fillers, colorants, and other additives which must be blended prior to their use in the transfer molding process as shown in Figure 49. The blended material is usually formed into a preform of specific weight prior to its use. A more detailed description of blending methods can be found in the Compounding section of this document.

Preforms are preheated by heat lamps, hot air ovens, or more commonly, dielectric heaters. The material is then put into a chamber or "transfer pot" where it is plasticized by heat and pressure into a viscous mass. When molded, the plastic is forced through the sprues and runners into the mold cavity. The pot, sprues, runners, and cavity surfaces are maintained at a temperature suitable for rapid curing of the material. The plastic is held in the mold at its cure temperature until the part is capable of maintaining its shape.

Since the polymer charge is injected into the mold near its curing temperature, the curing time in the mold is significantly reduced from that required in compression molding. While a form is being cured in the mold, a new polymer charge can be heated in the transfer pot. The mold is opened and the part is released by ejector pins. The sprues, runners, and the plastic remaining in the pot are also removed and become thermoset scrap. Very little flash is present on transfer molded products and they, therefore, require less trimming and finishing than those items produced by compression molding.

There are three variations on the basic transfer molding process distinguished by the manner in which the material is forced from the pot into the mold cavity. They are: integral pot-type, plunger-type, and screw-type. In integral pot transfer molding, the thermosetting material is forced into the mold cavities by pressure. In plunger transfer molding, the plastic material is forced from the pot to the mold cavities by a ram operated plunger. Generally, plunger transfer molding develops more frictional heat than pot transfer molding and reduces molding cycle time. In screw transfer molding, a reciprocating screw, similar to that which can be used in injection molding, is used to plasticize the molding powder. As the plastic material builds up at the end of the screw, it forces the screw to move backward. The screw then acts like a ram to force the material on through the runner system to the mold.

OPERATING PARAMETERS AND UTILITY REQUIREMENTS

The polymer formulation and the configuration of the part must be taken into consideration when determining what the molding temperature and pressure should be.

TABLE 91. TRANSFER MOLDED PRODUCTS

- Automotive ignition parts
- Brake pistons
- Camera and equipment cases
- Capacitors
- Circuit boards
- Circuit breakers
- Coils
- Connectors
- Detonators and caps
- Dinnerware
- Distributor caps
- Diodes
- Electrical sockets
- Ignition coils
- Insulators
- Integrated circuits
- Missile components
- Pump impellers
- Relays
- Resistors
- Solenoids
- Switch gears
- Terminals
- Tool and appliance handles
- Transformers
- Transistors
- Vacuum tube bases

Sources: Bikales, Norbert M. (ed). Encyclopedia of Polymer Science and Technology, Vol. 6, pp. 242-243.

Frados, Joel, ed., Plastics Engineering Handbook of the Society of the Plastics Industry, Inc., 1976, p. 233.

Grayson, Martin (ed). Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Edition, (Vol:pp) 2:451-452, 9:287, 17:408.

Schwartz, Seymour S. and Sidney H. Goodman, Plastics Material and Processes, 1982, pp. 692-696.

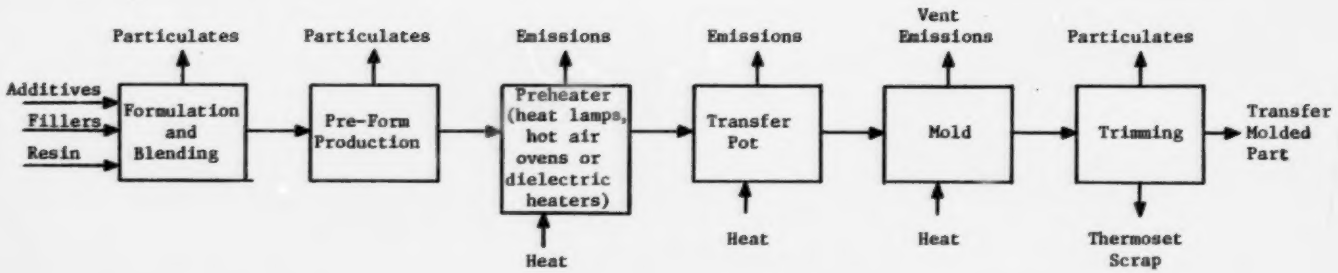
Additives
Fillers
Resin
Particulates
Formulation and Blending
Particulates
Pre-Form Production
Emissions
Preheater (heat lamps, hot air ovens or dielectric heaters)
Heat
Emissions
Transfer Pot
Heat
Vent Emissions
Mold
Heat
Particulates
Trimming
Thermoset Scrap
Transfer Molded Part

Figure 49. Transfer molding.

In transfer molding operations, the temperature and pressure are estimated and the actual parameters are then determined through trial runs. Temperatures range from 138 to 193°C (280 to 380°F) depending on the material characteristics, design of the mold, and geometry of the part.[151] The pressures necessary during compression molding range from 4.1 to 8.7 x 10^7 Pa (6,000 to 12,000 psi).[10] Table 92 presents typical temperatures and pressures used for thermoset resin formulations.

WASTE STREAMS AND EMISSIONS

Transfer molding operations produce air emissions and solid waste. No wastewater is produced since water is not used in the transfer molding process. Table 93 presents a summary of the point source emissions during transfer molding operations. More detailed information on the waste streams and emissions from major plastics additives used in transfer molding is presented in the Industry Description section of this document.

Air Emissions - Transfer molding operations have the potential to produce particulate and hydrocarbon emissions. Particulates are produced from the polymer formulation, blending, and preform production. Particulates are also produced by the trimming of any flash found on the molded parts. These particulates consist of particles of polymer, fillers, and other additives.

Volatile emissions are liberated during the preheating of the preforms, as well as during the actual transfer molding cycle. Transfer pots and molds usually contain vents to allow for the release of gaseous emissions such as trapped air and gaseous cure by-products. The bulk of such volatiles escape during the heating cycle in the transfer pot before the material enters the mold. Volatile emissions liberated consist of traces of monomers, additives, and cure reaction by-products. Decomposition products are not formed since the processing temperatures do not reach those temperatures at which the polymer begins to decompose as shown in Table 94.

Solid Waste - Thermoplastic scrap generated by the trimming of product flash can usually be ground and recycled to the formulation and blending step. Excess scrap and particulates, as well as trimmed thermoset scrap, must be disposed of as solid waste. Since this waste is comprised primarily of inert plastic material it will pose no disposal hazards.

WORKER DISTRIBUTION AND EXPOSURE

Worker distribution requirements for transfer molding are similar to those for compression moldings, as shown below:

Unit	Workers/Unit/8-hour Shift
Formulation/Blending	0.5
Preform Production	0.5
Polymer Preheat	0.25
Polymer Transfer	0.25
Molding	0.5
Trimming	0.25

TABLE 92. TRANSFER MOLDING TEMPERATURES AND PRESSURES

Polymer	Temperature °C	Pressure Pa ($\times 10^7$)
Alkyd Resins	121 - 165	
putty		3.4 to 5.5
granular		4.8 to 8.3
Diallyl Phthalate	121 - 163	
fiber filled		5.5 to 6.9
glass reinforced		6.9 to 8.3
Epoxy Resins	143 - 180	
glass reinforced		0.7 to 1.4
mineral filled		0.7 to 1.4
Melamine Formaldehyde	138 - 177	
cellulose or mineral filled		5.5 to 8.3
glass reinforced		6.9 to 10.3
Phenolic Resins	143 - 177	
general grades		4.8 to 8.3
glass reinforced		6.9 to 8.3
macerated-fabric		8.3 to 10.3
Polyester Resins	88 - 149	
clay filled		0.7 to 3.4
glass reinforced		0.7 to 6.9

Source: Baird, R. J., Industrial Plastics, 1971, p. 131.

TABLE 93. TRANSFER MOLDING POINT SOURCE EMISSIONS

	Air Emissions							Solid Waste		
	Particulates			Volatiles						
	Polymer	Filler	Additives	Cure Reaction By-Products	Monomer	Additives	Decomposition Products	Filler	Polymer	Additives
Compounding/Blending	X	X	X		X	X				
Preform Production	X	X	X							
Preheaters					X	X				
Transfer Pot and Mold				X	X	X	X			
Trimming	X	X	X					X	X	X

TABLE 94. DECOMPOSITION PRODUCTS

Polymer	Highest Processing Temperature (°C)†	Decomposition Temperature (°C)§	Decomposition Products
Alkyd Resins	165	232	*
Diallyl Phthalate	163	225	*
Epoxy Resins	180	200	*
Melamine Formaldehyde	177	182	*
Phenolic Resins	177	300	*
Polyester Resins	149	275	*
Urea Formaldehyde	154	182	*

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*Decomposition products are not formed at or near transfer molding temperatures.

†This is the highest possible temperature reached by the normal transfer molding of all formulations of the polymer listed.

§This is the lowest temperature at which decomposition products begin to form.

Employees performing jobs in transfer molding operations may be exposed to the contaminants shown in Table 95.

Toxicity information for the contaminants in Table 95 is summarized in Appendix C of this document and IPPEU Chapters 10 and 10b.

TABLE 95. TRANSFER MOLDING EMISSIONS AND RELEASE POINT ESTIMATION

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Formulation/Blending	Fugitives	[1]Polymer Particulates - alkyds - amino resins - epoxies - phenolics - polyesters
		[2]Additive Particulates: Colorants - Cd sulfoselenide - phthalocyanines - monoazo yellow Flame Retardants - antimony oxide Reinforcers - glass fibers - asbestos - silica
		[2]Filler Particulates: Alkyds - antimony oxide - asbestos - clay - glass fibers - minerals - synthetic fabrics Epoxies - asbestos - glass fibers - metals - minerals - silica Phenolics - asbestos - cellulose - glass fibers - macerated fabrics - minerals

(continued)

TABLE 95 (continued)

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Formulation/Blending (continued)		Melamine - asbestos
		- cellulose
		- glass fibers
		- macerated fabrics
		- minerals
		Urea/Formaldehyde - cellulose
		Polyester - asbestos
		- cellulose
		- clay
		- glass fibers
		- minerals
		- synthetic fabrics
		^{3}Volatile Monomer - formaldehyde
		- urea
		- melamine
		- epichlorohydrin
		- bisphenol-A
		- phenol
		^{2}Volatile Additives
	Mixing Machines	Noise
Preform Production	Fugitives	^{1}Polymer Particulates
		^{2}Additive Particulates
		^{2}Filler Particulates
Preheaters	Heater Vents Fugitives	^{3}Volatile Monomer
		^{2}Volatile Additives

(continued)

TABLE 95 (continued)

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Transfer Pot/Molding Machine	Transfer Pot and Mold Vents	[3]Volatile Monomer
	Fugitives	[2]Volatile Additives
		[4]Cure By-Products
Trimming	Fugitives	[1]Polymer Particulates
		[2]Additive Particulates
		[2]Filler Particulates

[1] Polymers typically transfer molded. Other polymers may be formed this way for specialty applications.

[2] Major additives and fillers documented in the literature. Many other additives may be used, depending on product formulation specifications.

[3] Principal monomers used to produce the plastics typically formed via transfer molding. Other monomers or comonomers also may be present.

[4] Unspecified.

SECTION 19

REINFORCED PLASTICS

FUNCTION

Reinforced plastic products have found a wide range of uses in the automobile, construction, and industrial products markets. Such products are formed by combining the resin material with reinforcing agents. This combination allows parts to be designed which can be larger and stronger than non-reinforced parts. Properties such as chemical resistance, dimensional stability, electrical properties, heat resistance, and abrasion resistance are also improved.[185]

Most parts which are now commercially made of reinforced plastics were made of metals. Reinforced plastic parts offer a number of economic advantages over metal parts including savings in raw material, manufacturing, energy, and capital equipment costs.

A number of different reinforced plastics processes are commercially employed to produce reinforced products from thermoplastic and thermoset resins. They will be described in detail in the process description section. The processes are broken into four general types:

Open Mold Processing
Closed Mold Processing
Filament Winding
Pultrusion

The production of continuous reinforced laminate sheets is not discussed under the reinforced plastics heading, but is presented in Section 12 - Laminating.

INPUT MATERIALS AND END PRODUCTS

Polymers, reinforcing agents, and additives serve as the input materials to the reinforced plastics processes. The combination and blend of these materials must be carefully determined to arrive at the proper product characteristics.

Both thermoset and thermoplastic resins are utilized to produce reinforced plastics. Thermosetting resins have traditionally been the high volume polymers used in reinforced molding. Unsaturated polyester has been the leading volume resin since it provides good strength, comparatively low cost, and can cure at room temperature. Epoxies, phenolics, and amino resins are also used extensively in reinforced molding.[185]

Thermoplastic resin can be purchased by the reinforced plastics processor in three forms: pellets into which the reinforcing fibers have already been compounded; concentrate pellets with a high percentage of reinforcement material; and plain polymer powder for the processor to specifically compound prior to processing. Polypropylene and nylon are the most commonly used thermoplastic resins. Shown below is a list of the thermoset and thermoplastic resins which are commercially used in reinforced plastics processing:

Thermosets	Thermoplastics
Acrylic Resins	Acrylonitrile-Butadiene-Styrene (ABS)
Alkyd Resins	Engineering Thermoplastics
Diallyl Phthalate (DAP)	Fluoropolymers
Epoxy Resins	Nylons
Melamine Formaldehyde	Polyacetal
Phenolic Resins	Polycarbonate
Polyurethane	Polyester (Thermoplastic)
Unsaturated Polyester	Polyethylene
	High Density
	Low Density
	Linear Low Density
	Polypropylene
	Polystyrene
	Styrene-Acrylonitrile (SAN)

Reinforcing agents must be carefully chosen for each formulation and application. They can be fibrous, powdered, spherical, or crystalline and can be organic, inorganic, metallic, or ceramic material. Ninety percent of all fibers used in reinforced plastics are composed of glass.[130] Glass formulations such as chemical resistant, high strength, and electrical grades are produced for specialty applications. There must be a strong adhesive bond between the resin and the reinforcements in order to give maximum strength to the part. Coupling agents are often used to enhance the polymer-filler surface bonds thereby increasing the ability of the composite to retain its original properties after prolonged use.

Glass fibers are available in many forms including woven fabric, nonwoven mats, bulk-chopped and milled fibers, and yarns. Glass microballoons or spheres are sometimes used for specialty applications.

A typical formulation used for reinforced plastics was not found in the literature; however, the typical percentage of glass used for reinforcement of commercial thermoplastics is listed below:[82]

Resin	Percent Glass Reinforcement
Acrylonitrile-Butadiene-Styrene	30
Polyacetals	20
Nylon 6	30
Nylon 66	30
Nylon 610	30

Resin	Percent Glass Reinforcement
Nylon 612	33
Fluorinated Ethylene Propylene	30
Polycarbonates	20
Polyester Thermoplastic	30
High Density Polyethylene	30
Polypropylene	20
Polystyrene	20
Styrene-Acrylonitrile	20

Other commonly used reinforcing agents are asbestos, sisal (cellulosic), and cotton fibers. Specialty applications use reinforcers such as carbon black, graphite, and boron whiskers. Asbestos is usually used in the form of loose fiber, paper, yarn, felt, or cloth. It is often used in conjunction with glass fibers particularly with polyvinyl chloride, polyesters, and polypropylene. Graphite and carbon black yarns add stiffness and rigidity to parts. They are used in injection molded nylon tennis rackets and in filament wound epoxy golf club shafts. Boron filaments have outstanding tensile strengths and have been used as reinforcers primarily in the aerospace and aircraft industry. Natural and synthetic fibers include nylon, rayon, cotton paper, and sisal. They provide low cost reinforcement in parts which require only intermediate strengths.

Additives must also be incorporated into the polymer-reinforcing agent blend in order to arrive at the proper plastic characteristics for the final product. Fillers, release agents, coupling agents, and colorants are most often used. Fillers are primarily used to reduce cost and only when the reinforcement content is low (50 percent or less).[72] Catalysts or cure agents are used in conjunction with the thermoset resins. Coupling agents improve the bond between the plastic and reinforcing agent. The choice of additives used for resins in cold mold processing of reinforced plastics is dictated by the polymer, process, and the intended end use. More information on typical additives used with these plastics is presented in the sections on Compression, Transfer, Injection and Reaction Injection Molding.

Typical high volume products of the reinforced molding processes include automobile parts and bodies, ceiling and wall panels, aircraft sections, boats, safety helmets, and large containers and tanks. Table 96 presents a list of the input materials and products used for the reinforced plastics processes. More detailed information on major plastics additives used in reinforced plastics is presented in the Industry Description section of this document. In particular, environmental and worker health concerns for exposure to fibrous glass, asbestos and silica are highlighted.

PROCESS DESCRIPTION

Reinforced plastics can be produced by a variety of processes and techniques depending upon the resin utilized and the end use product requirements. They can be characterized by four process types:

TABLE 96. REINFORCED PLASTICS INPUT MATERIALS AND END PRODUCTS

Process	Input Materials	Products
CLOSED MOLD PROCESSING		
Compression Molding	Unsaturated polyester Nylon 6 sheets Polypropylene sheets Glass fibers Asbestos Alpha cellulose Aramid Carbon fibers	Large components for automotive, appliance, and electrical hardware Lawn mower parts Seat backs Sound baffles Aircraft brake systems
Transfer Molding	Diallyl phthalate Epoxy Melamine-formaldehyde Phenolic resins Unsaturated polyester Glass fibers Asbestos Alpha cellulose Aramid	Aircraft parts Appliance housings Circuit boards Decorative parts Electrical components Pot handles Tool housings
Injection Molding	ABS Engineering Thermoplastics Fluoropolymers Nylon Polyacetal Polycarbonate Polyester (thermoplastic) Polyethylene Polypropylene Polystyrene SAN Glass fibers Asbestos Silica Carbon fibers Aramid Alpha cellulose	Appliance components Automotive grill openings Electrical applications Tennis rackets Hardware Cookware Static dissipators for copy machines Corrosion resistant molded pipe

(continued)

TABLE 96 (continued)

Process	Input Materials	Products
Reaction Injection Molding	Polyurethane Glass fibers Glass mat Wallastonite Mineral fibers	Automotive parts such as fenders Building supplies such as fascia panels
OPEN MOLD PROCESSING		
Hand lay-up	Epoxy Unsaturated polyester Glass fibers Aramid Typical Additives: Catalysts Colorants Coupling agents Flame retardants Impact modifiers Lubricants UV stabilizers Viscosity modifiers	Boat hulls for canoes, kayaks, and sailboats Large complex parts Prototype models
Spray-up	Epoxy Unsaturated polyester Glass fibers Aramid Typical Additives: Catalysts Colorants Coupling agents Flame retardants Impact modifiers Lubricants UV stabilizers Viscosity modifiers	Agricultural troughs Air ducts Bath tubs Boats and recreational vehicles Chemical tanks Feed bins Machine covers Shower stalls Swimming pools

(continued)

TABLE 96 (continued)

Process	Input Materials	Products
Bag Forming	Inputs same as hand lay-up and spray-up	Boats Aircraft parts
FILAMENT WINDING	Epoxy or Polyester Glass fiber Aramid filaments Carbon fibers	Airfoil blades Gas cylinders Fans and vanes Golf club shafts Helicopter blades, spars and tail booms Low pressure vessels Missile cones and rocket nozzles Steering wheels Storage tanks Pipes for oil fields, chemical process industries, water distribution and sewage disposal
PULTRUSION	Vinyl esters Glass fiber Aramid Carbon fibers	Electrical applications Poles, booms, and rails Gratings and trays Stiff, strong rods, tubes and structural shapes

Sources: Agranoff, J. (ed). Modern Plastics Encyclopedia, 1981, pp. 170, 171, 172, 392, 394, 397, and 298.

DuBois, J. H. and F. W. John, Plastics, 1981, p. 342.

Hattori, K., "Reinforced Plastics," Encyclopedia of Polymer Science and Technology, Vol. 12, pp. 1-41.

McGarry, Frederick J., "Laminated and Reinforced Plastics," Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Edition, Vol. 13, pp. 968-978.

Open Mold Processing
Closed Mold Processing
Filament Winding
Pultrusion

Open Mold Processing is used for an estimated 40 percent of reinforced plastics.[207] This process involves cutting the reinforcing mat or fabric to fit the mold and then applying a thermoset resin to saturate the reinforcing material. Three types of open mold processing are commonly used: hand lay-up, spray-up, and bag forming. A block diagram of open mold processing is shown in Figure 50.

The hand lay-up process is the simplest and oldest of the reinforced plastics processing steps. The open mold is first treated with a mold release agent. A mat of fiber is placed in the mold and is manually coated with resin. A roller or squeegee is then used to smooth the resin coating and force out bubbles. Layers of fiber and resin are added to provide the desired thickness. A smooth color layer can be produced by applying a pigmented layer to the mold before beginning the lay-up process. Colorants can also be mixed directly with the resin. The product is then cured at room temperature or in an oven depending upon the resin requirements. Polyesters and epoxies are used to produce the majority of hand lay-up reinforced products.

In the spray-up process the mold is treated with a mold release agent and a fiber mat is placed on the mold. The resin is then applied with a spray gun. Additional fiber and resin layers are added and the resin is allowed to cure. In a variation of this process, chopped fibers and the resin are sprayed simultaneously onto the treated mold surface. This process is best used when the part has more defined cavities since the loose wet fibers conform more easily to almost any shape.

Bag forming processes can begin with either the hand lay-up or spray-up processes. However, prior to curing, a bag is fitted to the mold and either pressure or vacuum forces the bag against the coated mold surface. The bag aids in forcing out trapped air and provides a more uniform thickness and surface finish compared to the hand lay-up or spray-up product.

A form of open mold processing is sometimes used to produce preforms for use in the closed mold processes. Preforms closely resemble the final molded shape and ensure the correct distribution of reinforcing fibers in the final molded shape. Three preforming methods are commonly used: manual placement of fibers held in place by resin binders; multiple station, automatic preforming equipment where resins and fibers are sprayed on chambers; and a water slurry method which involves water slurrying fibers and resin for ease of application on a preforming screen where the water is removed by vacuum.

Closed Mold Processing is used for high speed production of plastic reinforced products. The types of processes used in closed mold processing are much the same as conventional molding operations. Thermoplastic and thermoset resins are used, with polyester, epoxy, nylon, and polypropylene sharing the largest portion of the closed mold processing market.

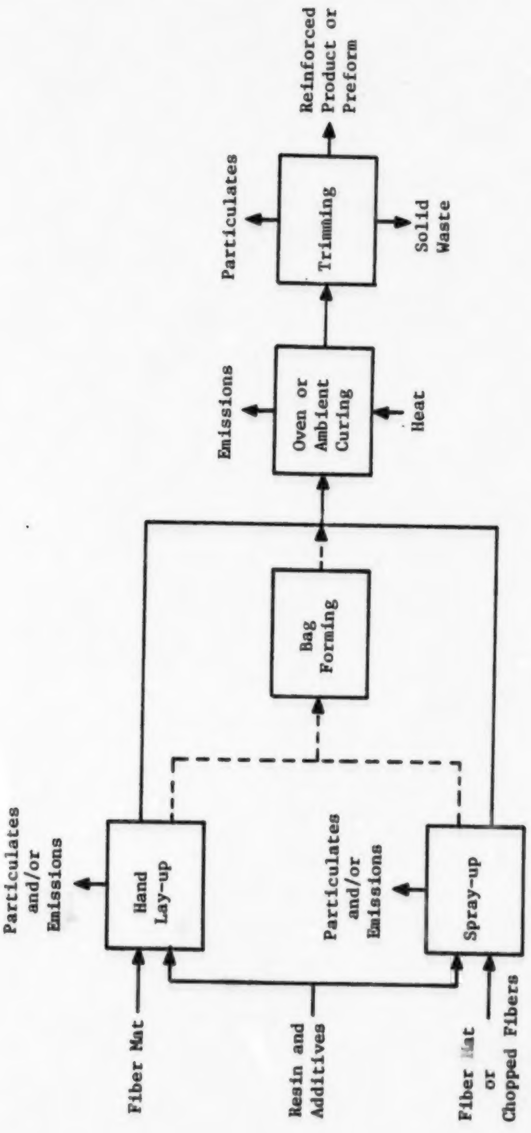

Fiber Mat
Resin and Additives
Fiber Mat or Chopped Fibers
Hand Lay-up
Particulates and/or Emissions
Spray-up
Particulates and/or Emissions
Bag Forming
Oven or Ambient Curing
Emissions
Heat
Trimming
Particulates
Solid Waste
Reinforced Product or Preform

Figure 50. Open mold processing.

Typical closed mold products include truck hoods, auto parts, luggage, appliance parts and trays and liners for refrigerated trailers. The advantages of closed mold processing include economy of high speed production, production of smooth finish and detail on all surfaces, and reproducibility of intricate detail and dimensions.

Four basic types of closed mold processing are commercially used: compression molding, transfer molding, injection molding, and reaction injection molding. The operation of these processes to produce reinforced products is very similar to those described in Sections 14, 15, 16, and 18 in this document for unreinforced products. A general block diagram of closed mold processing is shown in Figure 51 and a brief description of each process follows.

Compression molding is the most widely used closed mold process for processing thermoset resins. Most thermoset resins can be compression molded but the most commonly used are polyester and vinyl esters. The compression molding of reinforced plastics closely follows solid plastic compression molding except that the input includes reinforcing fibers along with the formulated plastic. Preforms are also used as input to the compression molding process. These preforms are often produced by an open mold process.

In compression molding, the fiber mat or preform is placed in the bottom half of the mold and the resin is added. The hydraulic press closes and the part is allowed to cure. The metal mold halves are sometimes heated to speed the cure and reduce production time. Some compression molding processes do not use a fiber mat or preform but instead fill the mold with a premeasured amount of a premixed resin-fiber-additive mixture.

Transfer molding can be used to mold reinforced thermoset resins into a single large part or a number of smaller parts. A mix of resin, reinforcers, and additives is charged into a transfer pot where it is heated. A plunger forces the charge through runners into the mold where the part is allowed to cure. This process is most commonly used to mold appliance housings from polyester and to mold electronic components from phenolic, DAP, and epoxy.

Injection molding is used for processing both thermoset and thermoplastic resins and it is the most commonly used method for forming reinforced themoplastic products. Ram or screw injection molding is used to force the resin-fiber-additive mix into a closed mold. The mold is heated to cure thermoset resins and is cooled to remove heat from thermoplastic parts. Polyester and most thermoplastics are processed by this method.

Reaction injecton molding is used to produce reinforced plastic products through the development of special processing equipment over the past few years. Polyurethane reinforced with milled glass is most commonly utilized. Wallastonite and other mineral fibers have been used to a lesser extent. Most reinforced reaction injection products find uses in the automotive industry.[119]

Filament Winding is a continuous process which involves wrapping fibers dipped in resin around a mandrel. The mandrel is either removed after the resin cures leaving a hollow shell, or it is left in place to form a permanent

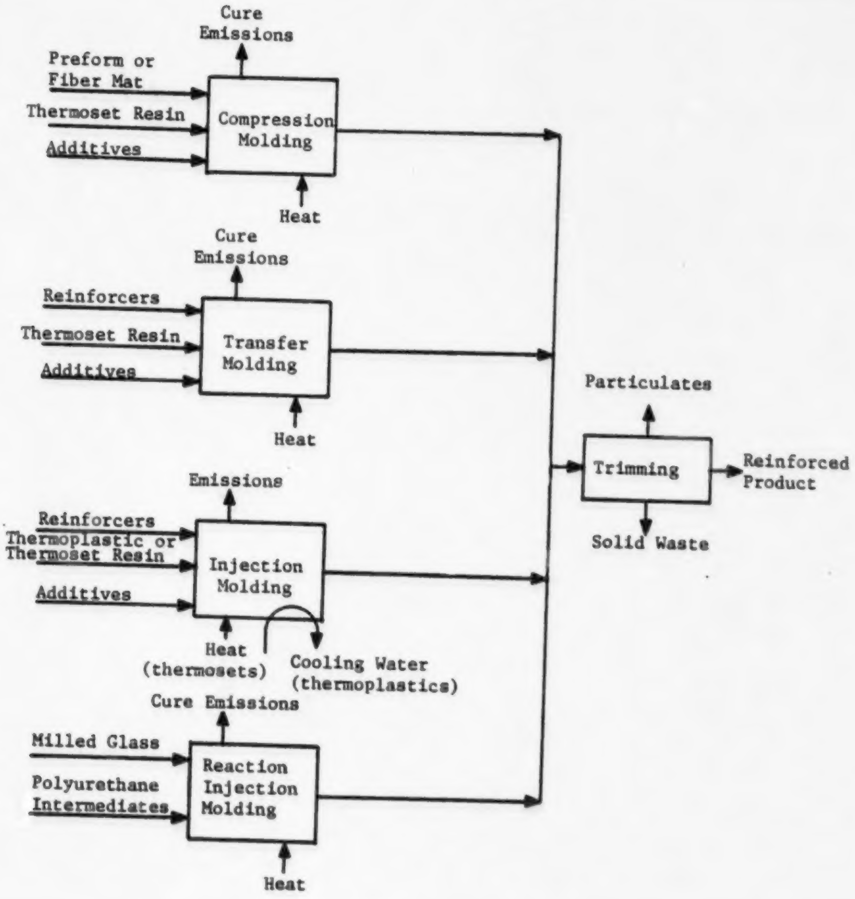

Cure Emissions
Preform or Fiber Mat
Thermoset Resin
Additives
Compression Molding
Heat
Cure Emissions
Reinforcers
Thermoset Resin
Additives
Transfer Molding
Heat
Emissions
Reinforcers
Thermoplastic or Thermoset Resin
Additives
Injection Molding
Heat (thermosets)
Cooling Water (thermoplastics)
Cure Emissions
Milled Glass
Polyurethane Intermediates
Reaction Injection Molding
Heat
Particulates
Trimming
Reinforced Product
Solid Waste

Figure 51. Closed mold processing.

liner. Figure 52 shows a block diagram of Filament Winding. Epoxy and polyester are the most commonly used resins for filament winding. Typical filament wound products include low pressure vessels, gas cylinders, storage tanks, and rocket nozzles.[15]

In this process, a continuous strand of fiber, usually glass, is drawn through an epoxy or polyester bath. The strand is then wound under tension around a rotating mandrel in a predetermined pattern which gives the part strength in the required directions. After the filament wound part has reached sufficient thickness it is cured at room temperature or in an oven.

Recent advances in filament winding allow for computer controlled winding which can wind from 24 to 67 m (80 to 220 feet) per minute of resin covered filament.[40]

Continuous Pultrusion is a unique reinforced plastics process which currently comprises less than 5 percent of the total reinforced plastics production.[202] The pultrusion products have specialty applications as replacements for profile metal products. Applications include fishing rods, ladders, rails, and gratings. Polyester and epoxy are most commonly used in this process along with glass fiber reinforcements. Carbon and aramid reinforcements are now being used in a number of commercial applications.

As shown in Figure 53, in continuous pultrusion glass fiber is drawn through a resin bath. It is then pulled through a heated steel die of the desired cross-sectional shape. The strand cures either in the die or by way of heat after the die. It is then cut into lengths according to its product requirement.

OPERATING PARAMETERS AND UTILITY REQUIREMENTS

The conditions under which reinforced plastics operations are performed are strongly governed by the polymer and reinforcements being processed and the end product application.

All of the open-mold processes along with filament winding and pultrusion are performed at atmospheric pressure. Pressures of 3.4×10^5 Pa (50 psi) are used during pressure bag forming.[87] The closed mold operations use pressure settings similar to those used during non-reinforced processing. Pressures range from 1 to 9×10^7 Pa for compression, transfer, and RIM molding and from 8 to 14×10^7 Pa for injection molding.

Reinforced thermoset operations usually do not require high temperatures to effect sufficient cures. Many of these operations allow the part to ambient cure. When a heating oven is used to speed the cure, temperatures are usually no higher than 175°C.[4] The closed mold processing of reinforced thermoplastic requires that the polymer be heated to temperatures which allow them to flow into the injection mold cavities. Table 97 shows the temperature ranges commonly used during the injection molding of reinforced thermoplastics. These temperatures are generally somewhat higher than those required during non-reinforced injection molding due to the presence of the reinforced fibers which reduce the polymer's flow properties.

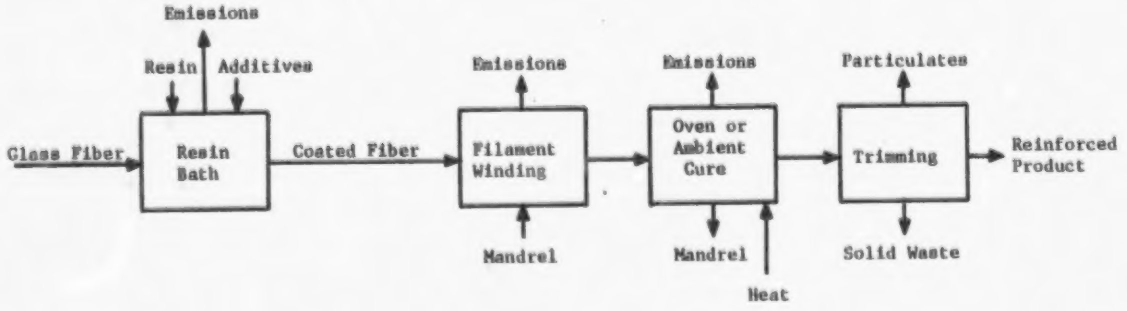

Emissions
Resin
Additives
Glass Fiber
Resin Bath
Coated Fiber
Emissions
Filament Winding
Mandrel
Emissions
Oven or Ambient Cure
Mandrel
Heat
Particulates
Trimming
Solid Waste
Reinforced Product

Figure 52. Filament winding.

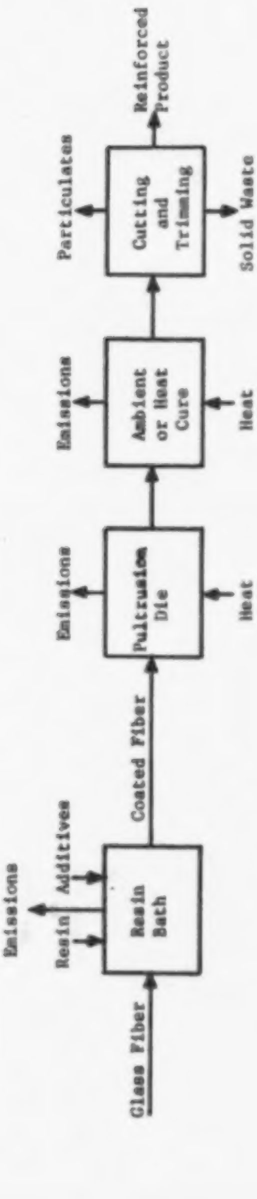

Glass Fiber
Resin
Emissions
Additives
Resin Bath
Coated Fiber
Emissions
Pultrusion Die
Heat
Emissions
Ambient or Heat Cure
Heat
Particulates
Cutting and Trimming
Solid Waste
Reinforced Product

Figure 53. Continuous pultrusion.

TABLE 97. REINFORCED CLOSED MOLD PROCESSING INJECTION MOLDING TEMPERATURES

Polymer	Molding Temperature °C
Acrylonitrile-Butadiene-Styrene (ABS)	260 - 288
Acetal Resins	170 - 210
Modified Polyphenylene Oxide and Polyphenylene Sulfide	315 - 330
Fluoropolymers	260 - 330
Nylon	288 - 343
Polycarbonate	302 - 323
Thermoplastic Polyester	232 - 266
Polyethylene	254 - 316
Polypropylene	271 - 296
Polystyrene	246 - 295
Styrene-Acrylonitrile (SAN)	232 - 288

Source: Hattori, K., "Reinforced Plastics," Encyclopedia of Polymer Science and Technology, Vol. 12, pp. 1-41.

WASTE STREAMS AND EMISSIONS

Reinforced plastics operations produce air emissions and solid waste. Wastewater is not produced since water is not directly used in the reinforced plastics processes. Any wastewater formed would be due to general equipment cleaning. Table 98 presents a summary of the point source emissions from reinforced plastics operations. All four processes produce particulates, volatile emissions, and solid waste. Emissions and wastes are discussed in more detail in the text below. The major plastics additives which contribute to waste streams and emissions are presented in more detail in the Industry Description section of this document.

Air Emissions - All of the reinforced plastics operations produce particulates and volatile emissions. Particulates are formed during the cutting and trimming of reinforced products and are comprised of polymer, additives, and reinforcer particles. Similar composition particulates are also generated during the handling of the solid resins, additives, and fibers prior to processing. Proper mixing equipment and techniques should keep particulate emissions to a minimum. Particulates are controlled by various standard control devices such as fiber filters and wet scrubbers.

Volatile emissions occur during the curing of thermoset products or during the heating of thermoplastic products. Thermoset cure emissions are liberated during all of the open mold processes, closed mold processes, filament winding, and pultrusion. Such emissions may contain volatilized monomer, additives, and cure reaction by-products. The injection molding processing of thermoplastic products will also generate volatile emissions. Such emissions will be comprised of volatilized monomer, additives, and decomposition products. Decomposition products occur when excess heat causes the polymer to decompose. Table 99 presents the decomposition products which may be formed during the injection molding of reinforced thermoplastic products.

Solid Waste - Thermoplastic and thermoset scrap is generated by the cutting and trimming of the reinforced products. Such scrap contains polymer, additives, and reinforcements. Excess thermoplastic scrap can often be ground and recycled to the injection molder feed; however, this must be done carefully because the overall efficiency of the material may be impaired. Thermoset scrap cannot be recycled and must be disposed of as solid waste. Solid waste produced by the reinforced plastics processes should pose no hazardous disposal problems since it is comprised of primarily inert plastic material and reinforcements.

WORKER DISTRIBUTION AND EXPOSURE

Open mold processing of reinforced plastics is employee-intensive because reinforcing agents are loaded manually into the open molds. Closed mold manpower requirements are similar to those for each of the four closed mold processes: compression, transfer, injection and reaction injection molding. Filament winding and pultrusion are simpler processes requiring less employee attention. Worker distribution for each of the above processes is given in Table 100.

TABLE 98. REINFORCED PLASTICS POINT SOURCE EMISSIONS

	Air Emissions							Solid Waste		
	Particulates			Emissions						
	Polymer	Additives	Reinforcements	Monomer	Additives	Cure Reaction By-Products	Decomposition Products	Polymer	Additives	Reinforcements
Open Mold Processing	X	X	X	X	X	X		X	X	X
Closed Mold Processing	X	X	X	X	X	X	X	X	X	X
Filament Winding	X	X	X	X	X	X		X	X	X
Pultrusion	X	X	X	X	X	X		X	X	X

TABLE 99. DECOMPOSITION PRODUCTS

Polymer	Highest Processing Temperature (°C)†	Decomposition Temperature (°C)§	Decomposition Products
Acrylonitrile-Butadiene-Styrene (ABS)	288	300	*
Acetal Resins	210	250	*
Modified Polyphenylene Oxide and Polyphenylene Sulfide	330	700	*
Fluoropolymers	330	300	HF
Nylon	343	300	CO, CO_2, NH_3, H_2O
Polycarbonate	323	330	*
Thermoplastic Polyester	266	300	*
Polyethylene	216	100	Ketone carbonyl groups form due to oxidation
Polypropylene	296	300	*
Polystyrene	295	300	*
Styrene-Acrylonitrile (SAN)	288	300	*

---

*Decomposition products are not formed at or near extrusion processing temperatures.

†This is the highest possible temperature reached by normal reinforced plastics operations for all formulations of the polymers listed.

§This is the lowest temperature at which decomposition products begin to form.

TABLE 100. ESTIMATED WORKER DISTRIBUTION IN REINFORCED PLASTICS PRODUCTION

Operation	Unit	Workers/Unit/8-hour Shift
Open Mold Processing	Hand Layup/ Sprayup	1.0
	Curing	0.5
	Trimming	0.25
Closed Mold Processing	Compression Molding	2.25
	Transfer Molding	2.25
	Injection Molding	1.5
	Reaction Injection Molding	1.625
Filament Winding	Resin Bath	0.25
	Filament Winding	0.25
	Curing	0.5
	Trimming	0.25
Pultrusion	Resin Bath	0.25
	Pultrusion Die	0.25
	Curing	0.5
	Cutting/Trimming	0.25

Employees assigned to open mold operations will have a higher exposure potential (particularly for additives and fillers manually applied as reinforcing agents) than those employed in more automated operations. Probable release points and contaminants have been estimated and are shown in Table 101. Toxicity information is summarized in Appendix C and discussed in detail in IPPEU Chapters 10 and 10b.

TABLE 101. REINFORCED PLASTICS EMISSIONS AND RELEASE POINT ESTIMATION

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Open Mold Processing		
Hand Layup/Sprayup	Fugitives	[1]Additive and Reinforcer Particulates:
		Flame Retardants - antimony oxide
		- trixylenyl phosphate
		Reinforcers - glass fiber
		- asbestos
		- silica
		Fillers - sisal
		- cotton fibers
		- carbon black
		- graphite
		- boron whiskers
		- glass balloons
		- synthetic fibers
		[2]Volatile Monomer - caprolactam
		- hexamethylenediamine
		- ethylene oxide
		- ethylene glycol
		- dimethylterephthalate
		- terephthalic acid
		- ethylene
		- 1-butene
		- 1-hexene
		- 1-octene
		- vinyl acetate
		- methyl methacrylate
		- epichlorohydrin
		- bisphenol-A
		- formaldehyde
		- melamine

(continued)

TABLE 101 (continued)

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Hand Layup/Sprayup (continued)		- urea - phenol - polyether polyols - acrylonitrile - 1,3-butadiene - styrene - 2,6-xylenol - p-dichlorobenzene - fluorocarbons - propylene
		[1]Volatile Additives
Curing	Oven or Curing Chamber Vent	[2]Volatile Monomer
	Fugitives	[1]Volatile Additives
		[3]Cure By-Products
Trimming	Fugitives	[1]Polymer Particulates
		[2]Additive and Reinforcer Particulates
	Trimming Tools	Noise
Closed Mold Processing		
Compression Molding	See Table 76.	
Transfer Molding	See Table 95.	

(continued)

TABLE 101 (continued)

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Injection Molding	See Table 82.	
Reaction Injection Molding	See Table 85.	
Filament Winding		
Resin Bath	Fugitives	[3]Volatile Monomer - epichlorohydrin - bisphenol A
		[1]Volatile Additives
		Glass Fibers
Filament Winding	Fugitives	[3]Volatile Monomer - epichlorohydrin - bisphenol A
		[1]Volatile Additives
		Glass Fibers
Curing	Oven or Curing Chamber Vents Fugitives	[3]Volatile Monomer - epichlorohydrin - bisphenol A
		[1]Volatile Additives
Trimming	Fugitives	[4]Polymer Particulates - epoxies - polyesters
		[2]Additive and Reinforcer Particulates
	Trimming Tools	Noise

(continued)

TABLE 101 (continued)

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Pultrusion		
Resin Bath	Fugitives	[3]Volatile Monomer - epichlorohydrin - bisphenol A
		[1]Volatile Additives
		Glass Fibers
Pultrusion Die	Die Head Fugitives	[3]Volatile Monomer - epichlorohydrin - bisphenol A
		[1]Volatile Additives
		Glass Fibers
Curing	Oven or Curing Chamber Vent Fugitives	[3]Volatile Monomer - epichlorohydrin - bisphenol A
		[1]Volatile Additives
Cutting/Trimming	Fugitives	[4]Polymer Particulates - epoxies - polyesters
		[2]Additive and Reinforcer Particulates
	Trimming Tools	Noise

[1] Major additives and reinforcing agents listed are documented in the literature. Other compounds may be present.

[2] Primary monomers used to produce polymers formed by open mold processing. Other monomers or comonomers may be present.

[3] Monomers from which epoxies are produced. A variety of unsaturated acids/anhydrides are used to produce polyester. See IPPEU Chapter 10, Section 15.

[4] Polymers typically formed are epoxies and polyesters.

SECTION 20

THERMOFORMING

FUNCTION

Thermoforming technology has been used since the turn of the century to shape cellulosic sheet into children's toys.[10] However, as a mass production process for shaping thermoplastics, thermoforming is a relatively new process and is rapidly expanding as new product applications are developed. Thermoforming is now a major processing technique of the plastics industry.

Thermoforming operations involve the heating of thermoplastic sheet or film to a pliable state and forcing it around the contours of a mold. Vacuum, air pressure, and/or mechanical force are employed to aid in the sheet forming. The cooled sheet retains the desired shape for products such as those used for housewares, light fixtures, and packaging products.

Thermoforming is one of the most cost effective and energy efficient processes for manufacturing a wide variety of plastic products.[28] The advantages of this process are: (1) high production rates of thermoformed parts versus equipment and tooling costs, (2) very high production rates for parts that are light and strong, and (3) lower production costs for thin wall thermoformed sections than those produced by way of injection molding.

INPUT MATERIALS AND PRODUCTS

Input materials to thermoforming operations are sheet and film produced by extrusion, calendering, casting, or foam operations. The solid or foam sheet and film can be laminated or printed prior to thermoforming. It is usually obtained by the thermoformer as ready to use formulated sheets or rolls. Some high volume thermoformers directly feed their thermoforming operations with sheet or film which they have captively produced by way of extrusion, calendering, or foam operations.

A wide variety of sheet and film plastic is suitable for thermoforming. The selection depends upon the requirements of the product including clarity, weatherability, toughness, flexibility, and color. Additives utilized prior to the formation of the sheet or film aid in the achievement of these requirements.

Table 102 presents a list of commonly thermoformed polymers and corresponding products. Also presented is a list of typical input sheet or film thickness. Engineering thermoplastics, linear low density polyethylene, and styrene-acrylonitrile are also thermoformed for specialty product applications.

TABLE 102. INPUT POLYMERS AND PRODUCTS OF THERMOFORMING OPERATIONS

Polymer	Typical Input Sheet Thickness (cm)	Products
Acrylic	1.25 (maximum)	lighting fixtures novelty furniture packaging signs and displays transportation parts
Acrylonitrile-Butadiene-Styrene (ABS)	0.013 - 0.635	airline serving pieces appliance parts automobile hoods and body parts computer covers luggage packaging refrigerator door liners
Polycarbonate	0.3 (maximum)	lighting fixtures transportation parts
High Density Polyethylene (HDPE)	0.025 - 0.318	automotive parts housewares industrial parts novelties packaging toys water tanks
Low Density Polyethylene (LDPE)	0.025 - 0.318	medical face masks packaging
Polypropylene	0.25 (maximum)	food containers housewares machine housing medical containers packaging plant pots

(continued)

Table 102 (continued)

Polymer	Typical Input Sheet Thickness (cm)	Products
Polystyrene High Impact and Foam	0.025 - 0.635	appliance parts housewares lighting fixtures novelties packaging drinking cups egg cartons fast food containers meat and poultry trays transportation parts toys
Polyvinyl Chloride (PVC) Rigid	0.005 - 0.152	contour maps lighting fixtures packaging signs and displays

Sources: Agranoff, J. (ed). Modern Plastics Encyclopedia 1981-1982, pp. 4, 8, 46, 58, 80, 90, 100.

Bruins, P. F. (ed). Basic Principles of Thermoforming, 1971, pp. 10, 40.

Glanvill, A. B., Plastics Engineer's Data Book, 1973, p. 139.

Levy, S. and H. DuBois, Plastics Product Design Engineering Handbook, 1977, p. 179.

A formulation for rigid PVC foil useful for deep draw thermoforming is as follows:[158]

Material	Parts by Weight
PVC/PVAc Copolymer (Corvic R51/83) (10% PVAc)	100
Barium/Cadmium/Zinc Stabilizer (Lankro Mark Q 152)	3
Epoxy Stabilizer (Paraplex G62)	3
Stearic Acid (lubricant)	0.5

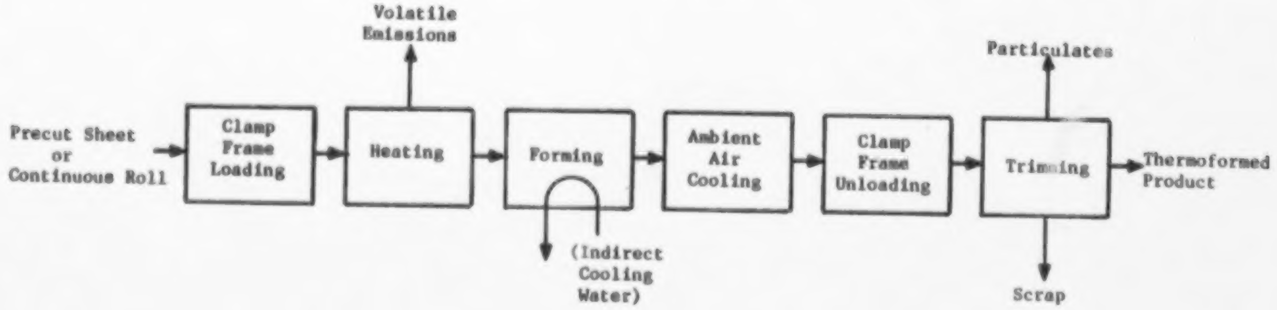
PROCESS DESCRIPTION

A block diagram of the series of operations which comprise thermoforming is shown in Figure 54. These operations are performed either as batch or continuous processes.[84] Batch processes are most often termed shuttle processes. These processes use pre-cut plastic sheets as input. The sheets undergo the entire series of thermoforming operations individually on a single piece of equipment. Shuttle processes are most often used for short production runs of large specialty parts such as car tops and boat hulls. Continuous processes accept both pre-cut sheets and continuous rolls of plastic sheet as input. Continuous thermoforming is performed at a series of production stations. These stations are often arranged in a rotary set-up where the frame clamped plastic sheet is rotated to the heating, forming, and cooling stations. Continuous operations produce such items as disposal cups, lids, plates, and packaging containers.[197]

Plastic sheet must be clamped into a frame prior to thermoforming in order to provide the heated plastic support throughout the entire process. The plastic sheet must be uniformly heated prior to being formed in order to be certain of uniform stretch during forming. One of three heating methods is usually used to bring the entire sheet gradually and evenly to its forming temperature: radiant heating, convection heating, and conduction heating.[15] Of these three, radiant heating is the most commonly used method and it is carefully controlled by a timed heating cycle. Thick sheets require the use of sandwich type heaters where infrared tubular heating elements with reflectors are placed on both sides of the sheet.[84]

When sufficiently heated, the plastic sheet is formed into the desired shape. One of the most attractive features of thermoforming is that relatively inexpensive molds can be used during forming due to the low pressures utilized. A variety of materials can be used for molds including wood, plastic, epoxy, urethane, phenolics, and metals. Wooden molds are generally used for prototypes or limited production runs. Cast aluminum is the most commonly used mold material for production runs since it provides a good combination of durability, light weight, and thermal conductivity.[31]

There are three major types of forming operations with a number of variations within each category. These three categories, (1) vacuum forming, (2) pressure forming, and (3) matched mold forming, are discussed below.


Precut Sheet
or
Continuous Roll
Clamp
Frame
Loading
Volatile
Emissions
Heating
Forming
(Indirect
Cooling
Water)
Ambient
Air
Cooling
Clamp
Frame
Unloading
Particulates
Trimming
Scrap
Thermoformed
Product

Parenthesis indicate that water is not used for all Thermoforming Operations.

Figure 54. Thermoforming.

Vacuum Forming is the most versatile of the thermoforming processes. A diagram of vacuum forming is presented in Figure 55. After heating, the soft and pliable sheet is placed directly above a concave mold and slight pressure is used to seal the plastic to the upper mold edge. Vacuum is applied from underneath through small holes in the mold cavity and atmospheric pressure forces the softened sheet against the mold contours from above.

Many variations of vacuum forming are commercially employed. One of these, drape forming, involves lowering a softened sheet clamped in a frame over a male mold. The sheet is stretched over the mold by the lowering motion and a vacuum applied from below draws the plastic against the mold. Another variation, called snap back forming, involves clamping a heated plastic sheet over a vacuum box. Vacuum is applied to draw down the plastic sheet into an arc. A convex mold is lowered into the cavity, the vacuum is released, and the plastic sheet "snaps back" to conform to the mold contour.

Plug assist vacuum forming involves sealing a heated plastic sheet across the top of a concave mold. Air is used to blow the sheet up into a bubble. A plug is used to plunge the plastic sheet into the mold and vacuum is applied to draw the sheet against the mold. Plug assist vacuum forming produces products with more uniform thickness than straight vacuum forming.

Pressure Forming, sometimes called blown air forming involves the use of air pressure to force the softened plastic sheet against the mold. A diagram of pressure forming is presented in Figure 56. Thermoplastic sheet is clamped over a concave mold and is usually softened by radiant heat. The hot sheet is covered and compressed air is blown through openings in the cover. The air pressure forces the sheet against the mold contours. Vent holes in the mold allow trapped air to escape.

Mechanical plugs are sometimes used to aid in pressure forming by distributing the material before the air pressure is applied. Vacuum is used to evacuate the space between the plastic sheet and the mold so as not to trap air in the final product.

A variation of pressure forming is called free blowing. A sheet is clamped over a pressure box which has an opening of the shape required by the product. After the sheet is softened, compressed air is forced from the pressure box causing the sheet to form a bubble. An indicator located on top of the bubble shuts off the air pressure when the desired height is reached.

Matched Mold Forming is particularly suitable for products requiring excellent reproduction detail. A diagram of matched mold forming is presented in Figure 57. Convex and concave mold halves, which fit together perfectly, are used in this forming process to shape softened thermoplastic sheet. The molds are usually made of aluminum or steel with the mold surfaces being highly polished or textured since both halves contact the sheet surface. The heated sheet material is placed between the molds and the press is either hydraulically or pneumatically closed. Vents in the mold allow trapped air to escape from the mold product. The mold is normally water-cooled to control mold temperatures and to allow for sufficient part cooling.

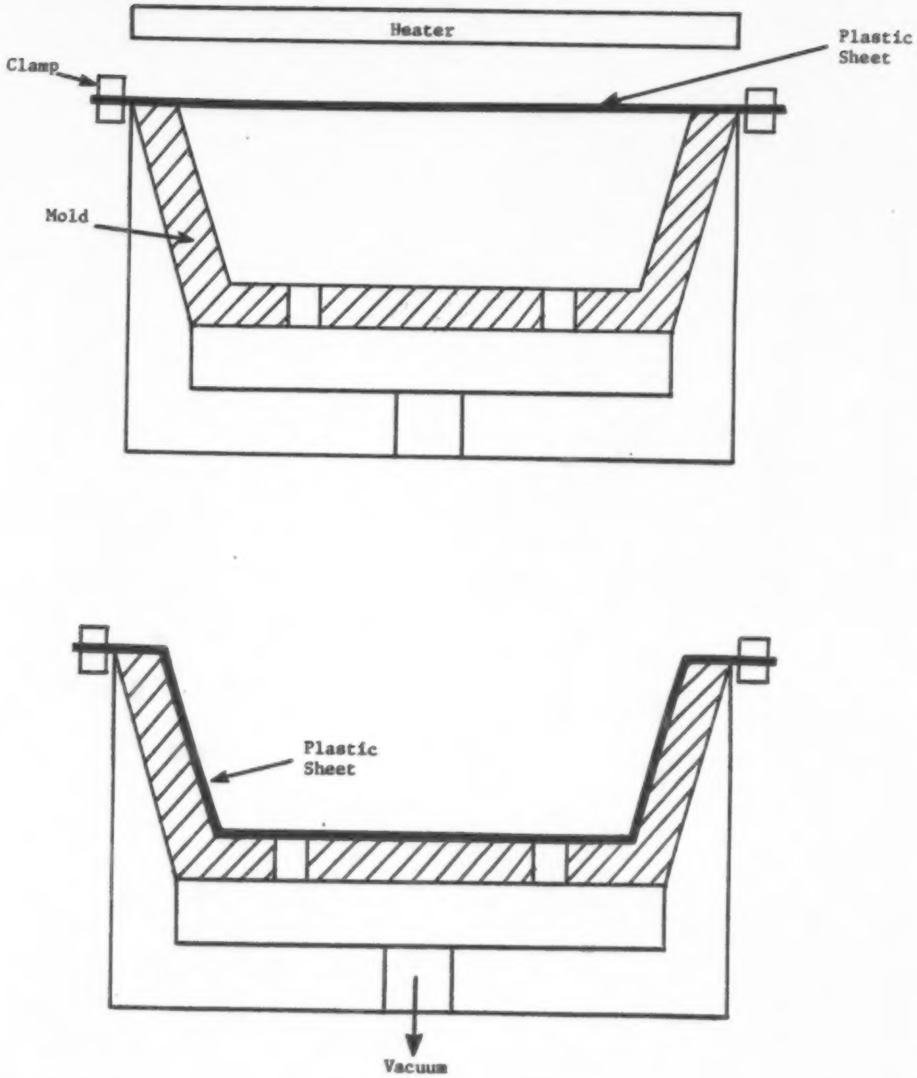

Heater
Plastic Sheet
Clamp
Mold
Plastic Sheet
Vacuum

Figure 55. Vacuum forming.

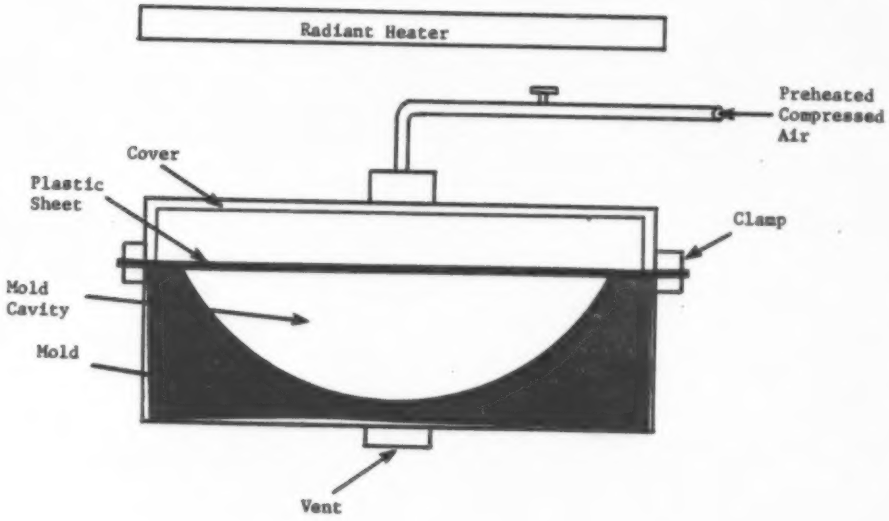

Radiant Heater
Preheated
Compressed
Air
Cover
Plastic
Sheet
Clamp
Mold
Cavity
Mold
Vent

Figure 56. Pressure forming.

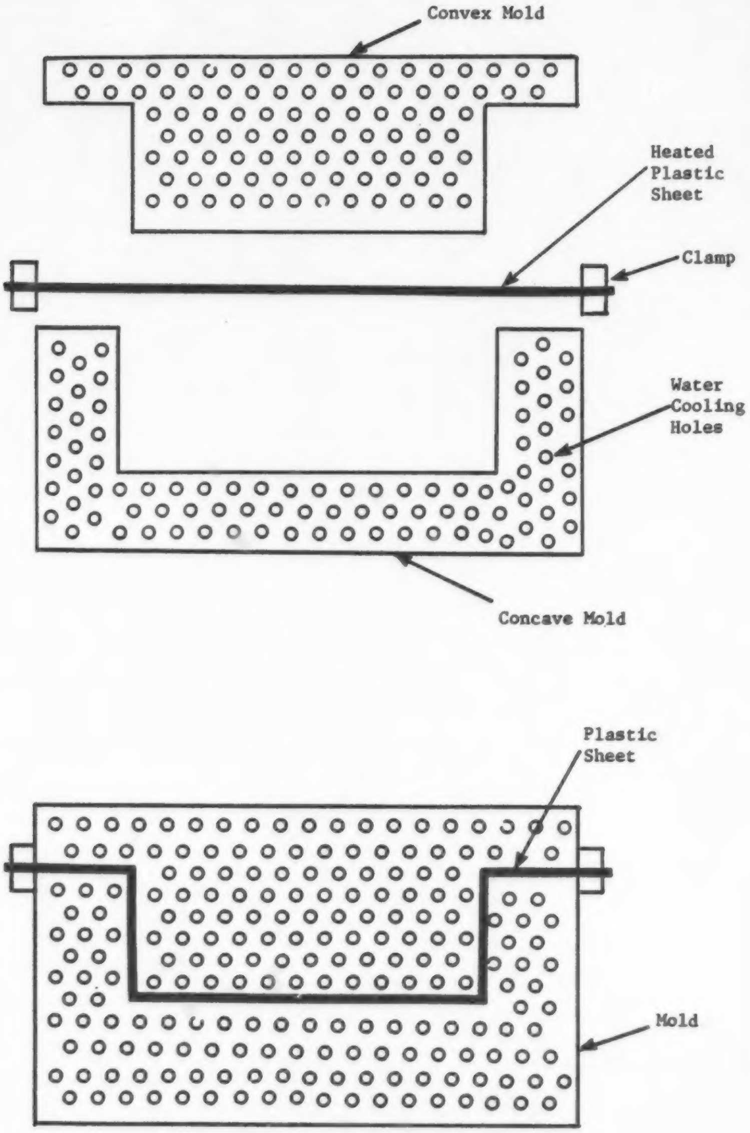

Convex Mold
Heated Plastic Sheet
Clamp
Water Cooling Holes
Concave Mold
Plastic Sheet
Mold

Figure 57. Matched mold forming.

The initial phases of cooling occur while the formed sheet still surrounds the mold. Shrinkage does occur during such cooling thereby facilitating sheet removal from the mold. Air ejection is often used for this purpose.[84] Thermoformed parts are then ambient air cooled. The cooling phase of thermoforming accounts for most of the thermoforming cycle time. When sufficiently cooled, the formed sheet is unloaded from the clamp frame, and trimmed and decorated according to product specifications.

OPERATING PARAMETERS AND UTILITY REQUIREMENTS

Table 103 illustrates the range of temperature used in thermoforming operations. The set temperature is that temperature at which the part may be removed from the mold without warpage. The lower processing limit represents the lowest temperature at which the material can be formed without creating undue stresses. The normal forming temperature is that temperature at which the sheet should be formed under normal operation. This temperature must be reached throughout the entire sheet. The temperature point where the thermoplastic sheet begins to degrade or become too fluid and pliable to thermoform is termed the upper limit. Molds used during thermoforming have temperatures between the mold temperature range.[31, 83]

The forming air pressure used during pressure forming biaxially oriented polystyrene ranges from 5.5 to 8.3 x 10^5 Pa (80 to 120 lb/in^2).[83]

WASTE STREAMS AND EMISSIONS

Thermoforming operations produce air emissions and solid waste. No wastewater is generated by thermoforming operations. Fugitive particulates and volatile emissions represent the only potential area of environmental concern associated with thermoforming.

Table 104 presents a summary of the point source emissions from thermoforming operations. Emissions and wastes are discussed in more detail in the text below.

Air Emissions - Thermoforming operations have the potential to produce volatile emissions and particulates. Volatile emissions may be liberated during the heating cycle. Such emissions would be comprised of volatilized plasticizers and decomposition products. Decomposition products occur when excess heat causes the polymer to decompose. Table 105 presents a table of decomposition products which can occur when the various thermoforming input polymers are exposed to high temperatures. Temperatures above which decomposition products are likely to be formed are also listed. Stabilizers are usually included in sheet formation to inhibit decompositon product formation and plasticizers are usually chosen which do not volatilize easily at the process temperature.

Particulates are produced during the trimming of thermoformed sheet. These particulates consist of polymer, plasticizer, and colorant particles. Particulates can be controlled by various standard control devices such as fabric filters and wet scrubbers.

TABLE 103. THERMOFORMING TEMPERATURES (°C)

	Set Temperature	Processing Temperature Lower Limit	Normal Forming	Upper Limit	Mold Temperature Range
Acrylic Resins	85	149	177	193	60 - 82
ABS	85	127	146	182	60 - 82
Polycarbonate	138	168	191	204	80 - 100
LDPE	†	120	135	165	60 - 80
HDPE	82	127	146	182	70 - 90
Polypropylene	†	150	†	180	70 - 90
Polystyrene	85	127	146	182	50 - 70
PVC	66	93	118	149	40 - 50

---

†Temperature data not found in the reference literature.

Sources: Bruins, P. F. (ed). Basic Principles of Thermoforming, 1971, p. 40.

Glanvill, A. B., The Plastics Engineer's Data Book, 1973, p. 137.

Grimes, J. F., "Thermoforming," Modern Plastics Encyclopedia 1981-1982, p. 405.

TABLE 104. THERMOFORMING POINT SOURCE EMISSIONS

	Air Emissions					Solid Waste		
	Particulates			Volatiles				
	Polymers	Plasticizer	Additives	Plasticizer	Decomposition Products	Polymer	Plasticizer	Additives
Heating				X	X			
Trimming	X	X	X			X	X	X

TABLE 105. DECOMPOSITION PRODUCTS

Polymer	Highest Processing Temperature (°C)†	Decomposition Temperature (°C)§	Decomposition Products
Acrylic Resins	193	320	*
ABS	182	300	*
Polycarbonate	204	#	*
Polyethylene	182	100	Ketone carbonyl groups form due to oxidation
Polypropylene	180	300	*
Polystyrene	182	300	*
PVC	149	100	HCl

---

*Decomposition products are not formed at or near thermoforming processing temperatures.

†This is the highest possible temperature reached by the normal thermoforming of all formulations of the polymer listed.

§This is the lowest temperature at which decomposition products begin to form.

#Temperature not found in the reference literature.

Wastewater - Thermoforming operations only utilize water in the indirect cooling of the forming molds. Therefore, no wastewater streams are expected to be produced by the thermoforming process. Wastewater may be produced if particulate emissions are controlled by wet scrubbing. Such a waste stream would contain suspended solids such as polymer, plasticizers, and colorants.

Solid Waste - A great deal of scrap thermoplastic sheet is produced by the trimming of thermoformed product. Scrap can run as high as 50 percent on some parts.[84] This scrap cannot be reused in thermoforming operations unless the processor also produces the input sheet. In these cases the scrap can be ground and processed with virgin resin to form sheet and film. Thermoform scrap can be sold to reprocessors who sort and resell the scrap to processors requiring lower grade input material for their processing operations. The disposal of most plastic scrap from thermoforming operations should present no problems since plastic scrap is characteristically inert.

WORKER DISTRIBUTION AND EXPOSURE

Thermoforming operations are automated and relatively simple. Employee manpower is concentrated in the operations of clamp frame loading and unloading and product trimming. Estimated worker distribution for thermoforming is shown below:

Unit	Workers/Unit/8-hour Shift
Clamp Frame Loading	0.5
Heating/Forming/Cooling	0.25
Clamp Frame Unloading	0.5
Trimming	0.25

Volatile emissions are possible when polymer sheet is heated prior to forming. Exposure to polymer and additive particulates may occur during product trimming. Estimated contaminants and release points are shown in Table 106. Toxicity information is summarized in Appendix C of this document and IPPEU Chapters 10 and 10b.

TABLE 106. THERMOFORMING EMISSIONS AND RELEASE POINT ESTIMATION

Operation Unit(s)	Release Point(s)	Chemical Substance or Physical Agent
Heating	Heater Vents Fugitives	[1]Volatile Plasticizer
		Decomposition Products - ketone carbonyls (polyethylenes) - HCl (polyvinyl chloride)
Trimming	Fugitives	[2]Polymer Particulates - acrylics - ABS - polyolefins - polystyrene - polyvinyl chloride
		[1]Plasticizer and Additive Particulates
	Trimming Tools	Noise

---

[1] Plasticizers and additives incorporated into polymer sheet during forming are unspecified. Most plasticizers are probably phthalates; a variety of additives may be used.

[2] Polymers typically thermoformed. Other polymers may be thermoformed for special applications.

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APPENDIX A. ADDITIVE USAGE INFORMATION FOR THE PLASTICS AND RESINS PROCESSING INDUSTRY

TABLE A-1. ADDITIVES USED IN THE PLASTICS AND RESINS PROCESSING INDUSTRY

Additive Class	Chemical	Polymer Application	Comments
Antioxidants	2,6-Di-tert-butyl-4-methyl phenol (BHT)	Acetals Polyester (Terephthalate) Polyester (Alkyds) Polyethylene Low Density Linear Low Density High Density Polypropylene GP Polystyrene Impact Polystyrene ABS Polyvinyl Chloride Polyvinylidene Chloride	1. FDA approved 2. Synergism with dilauryl 3,3'-thiodipropionate 3. In PVC, also acts as a costabilizer with conventional heat stabilizers 4. Has "generally recognized as safe" status
	Trisnonylphenyl phosphite	Polyester (Terephthalate) Polyester (Alkyds) Polyethylene Low Density Linear Low Density High Density Polypropylene Impact Polystyrene ABS Polyvinyl Chloride Polyvinylidene Chloride	1. FDA approved for Resinous and Polymeric Coatings (food packaging) 2. Acts as a plasticizer and costabilizer with conventional heat stabilizers in vinyls 3. Liquid at room temperature 4. Used in conjunction with phenolic antioxidants
	Dilauryl thiodiproprionate	Polyethylene Low Density Linear Low Density High Density Polypropylene GP Polystyrene ABS Polyvinyl Chloride Polyvinylidene Chloride	1. FDA approved for food packaging (less than 0.02%) 2. Acts as plasticizer softening agent, and costabilizier with conventional heat stabilizers in vinyls 3. Synergism with conventional antioxidants such as hindered phenols and sulfur compounds

(continued)

TABLE A-1 (continued)

Additive Class	Chemical	Polymer Application	Comments
Blowing Agents	Azodicarbonamide	Acetals Acrylics High Density Polyethylene Polypropylene ABS High Impact Polystyrene Polyvinyl Chloride	1. Sanctioned for use by FDA - residue is nontoxic 2. Can be stored and handled safely at room temperature 3. Non-combustible 4. May act as stabilizer
	Azobisisobutyronitrile	Acrylics GP Polystyrene Polyvinyl Chloride	1. Toxic residue (i.e., tetramethyl succinonitrile) 2. Flammable 3. Can be used as a catalyst in acrylic fiber spinning 4. Residue may act as a heat stabilizer in vinyls
	Methylene Chloride	Polyethylene Low Density Linear Low Density High Density GP Polystyrene ABS Polyurethanes	1. Market share is increasing due to replacement of fluorocarbons 2. Relatively safe for humans 3. Careful compounding required for polyurethanes
Colorants	Carbon black	Has application in virtually all plastics. Acetals Acrylics Amides Amino Resins Epoxy Resins Fluoroplastics Nylon 6 and 6/6 Phenolic Resins Polycarbonate Polyester (Terephthalate) Polyester (Alkyds) Polyethylene Low Density Linear Low Density High Density	1. Available as a powder, paste, or pellet 2. Also acts as a UV quencher, filler, antistatic agent, electrical insulator and reinforcer 3. Approved by the USDA for food packaging 4. Heat stability to 300°C. 5. Low extractability for plastics.

(continued)

TABLE A-1 (continued)

Additive Class	Chemical	Polymer Application	Comments
Colorants (Cont.)		Polypropylene GP Polystyrene Impact Polystyrene ABS Polyurethane Polyvinyl Acetate Polyvinyl Chloride Polyvinylidene Chloride	
	Titanium dioxide	Has application in virtually all plastics. Acetals Acrylics Amino Resins Epoxy Resins Fluoroplastics Nylon 6 and 6/6 Phenolic Resins Polycarbonate Polyester (Terephthalates) Polyester (Alkyds) Polyethylene Low Density Linear Low Density High Density Polyphenylene Sulfide Polypropylene GP Polystyrene Impact Polystyrene ABS Polyurethane Polyvinyl Acetate Polyvinyl Chloride Polyvinylidene Chloride	1. Rutile and anatase crystals 2. Sometimes used as a filler 3. Rutile crystal is abrasive and difficult to use in fiber spinning operations 4. Acts as stabilizer in polyolefins 5. Exempt from migratory testing for food packaging 6. Heat stability to 300°C

(continued)

TABLE A-1 (continued)

Additive Class	Chemical	Polymer Application	Comments
Colorants (Cont.)	Cadmium sulfoselenide	Acetals Acrylics Amino Resins Epoxy Resins Fluoroplastics Nylon 6 and 6/6 Phenolic Resins Polycarbonate Polyester (Terephthalate) Polyester (Alkyds) Polyethylene Low Density Linear Low Density High Density Polypropylene GP Polystyrene Impact Polystyrene ABS Polyurethane Polyvinyl Chloride	1. Toxic 2. Maroon pigment 3. Generally mixed with cadmium sulfide to give red, orange and maroon 4. Heat, alkali and weather resistant 5. Extremely insoluble 6. Not approved for food use 7. Heat stability up to 300°C
	Lead chromate	Acetals (C) Acrylics (C) Amino Resins Epoxy Resins Phenolic Resins Polyester (Terephthalate) Polyester (Alkyds) Polyethylene (C) Low Density Linear Low Density High Density Polypropylene (C) GP Polystyrene (C) Impact Polystyrene (C) ABS (C) Polyurethane Polyvinyl Acetate Polyvinyl Alcohol Polyvinyl Chloride	1. Toxic 2. Medium yellow 3. Mixed with lead oxide and other pigments to give orange, reds and greens 4. Thermally stable up to 200°C in plastics 5. Sensitive to acids, bases, and hydrogen sulfide 6. Migration resistant

(continued)

TABLE A-1 (continued)

Additive Class	Chemical	Polymer Application	Comments
Colorants (Cont.)	Phthalocyanines	Acetals Acrylics Amides Amino Resins Epoxy Resins Nylon 6 and 6/6 Phenolic Resins Polycarbonate Polyester (Terephthalate) Polyester (Alkyds) Polyethylene Low Density Linear Low Density High Density Polypropylene GP Polystyrene Impact Polystyrene ABS Polyurethane Polyvinyl Acetate Polyvinyl Chloride	1. Blues and greens 2. Difficult to disperse 3. Chlorination and bromination give yellows and greens 4. Many are approved by the USDA for meat and poultry contact 5. May retard curing of thermoset resins 6. May contain PCB's in concentrations greater than 50 ppm as impurities 7. Heat stability up to 280°C.
	Anthraquinone red Solvent red 111	Acrylics Nylon 6 and 6/6 Polycarbonate GP Polystyrene Impact Polystyrene ABS Polyurethane Polyvinyl Chloride	1. Superior weatherability 2. High price 3. Most commonly used in acrylics 4. Heat stability up to 518°F
	Monoazo yellow Solvent yellow 14	Acrylics Epoxy Resins Phenolic Resins Polyester (Alkyds) Polyethylene Low Density Linear Low Density High Density	1. Not recommended for processing over 150°C 2. Poor weatherability in acrylics 3. Widest use is in polystyrene, phenolics and polyvinyl chloride (rigid) 4. May tend to migrate in highly plasticized vinyls

(continued)

TABLE A-1 (continued)

Additive Class	Chemical	Polymer Application	Comments
Colorants (Cont.)		Polypropylene GP Polystyrene Impact Polyester ABS Polyurethane Polyvinyl Acetate Polyvinyl Chloride (rigid)	
Flame Retardants	Antimony oxide	Acrylics Epoxy Resins Phenolic Resins Polycarbonate Polyester (Terephthalate) Polyester (Alkyds) Polyethylene Low Density Linear Low Density High Density Polypropylene GP Polystyrene Impact Polystyrene ABS Polyurethane Polyvinyl Acetate Polyvinyl Chloride	1. Toxic 2. Commonly used as a synergist with halogenated compounds 3. Also acts as a filler for vinyls 4. Available in paste form to avoid dusting 5. May act as a pigment (whitening)
	Alumina trihydrate	Acrylics Epoxy Resins Phenolic Resins Polycarbonate Polyester (Terephthalate) Polyester (Alkyds) Polyethylene Low Density Linear Low Density High Density Polypropylene GP Polystyrene Impact Polystyrene ABS Polyurethane Polyvinyl Acetate Polyvinyl Chloride	1. Acts as smoke depressant and flame retardant 2. Commonly used as a filler 3. Acts as a nucleating agent in foams (commonly requires coupling agent) 4. Dehydration generally occurs around 290-300°C

(continued)

TABLE A-1 (continued)

Additive Class	Chemical	Polymer Application	Comments
Flame Retardants (Cont.)	Trixylenyl phosphate	Acrylics Epoxy Resins Polyester (Alkyds) GP Polystyrene Impact Polystyrene Polyurethane Polyvinyl Acetate Polyvinyl Chloride	1. Also acts as a plasticizer in PVC 2. Phosphorous promotes char formation and inhibits formation of combustible volatiles
	Decabromodiphenyl oxide	Acrylics Epoxy Resins Phenolic Resins Polyamides Polycarbonate Polyester (Alkyds) Polyethylene Low Density Linear Low Density High Density Polypropylene GP Polystyrene Impact Polystyrene ABS Polyurethane Polyvinyl Acetate Polyvinyl Chloride	1. Synergism with antimony oxide 2. Tends to reduce impact strength and increase UV sensitivity 3. Good thermal stability
	Chlorinated paraffin wax	Acrylics Epoxy Resins Polyester (Alkyds) Polyethylene Low Density Linear Low Density High Density Polypropylene GP Polystyrene Impact Polystyrene ABS Polyurethane Polyvinyl Acetate Polyvinyl Chloride	1. Generally contain 20-70% (by wt.) chlorine 2. Acts synergistically with antimony oxide 3. Inefficient plasticizers

(continued)

TABLE A-1 (continued)

Additive Class	Chemical	Polymer Application	Comments
Heat Stabilizers	Tribasic lead sulfate	Polyvinyl Chloride	1. Toxic 2. Wire and cable coating is main use 3. Low dusting formulations available
	Ba/Cd Stearate	Polyvinyl Choride Polyvinylidene Chloride	1. Toxic 2. Also acts as a lubricant 3. Solid
	Ca/Zn Stearate	Amino Resins Linear Low Density Polyethylene Polyvinyl Acetate Polyvinyl Alcohol Polyvinyl Chloride	1. Nontoxic 2. Many grades are FDA sanctioned 3. Also acts as a lubricant and light stabilizer 4. Available in solid, liquid or paste form 5. Amino resins uses this as a mold release agent 6. LLD Polyethylene utilizes additive as a catalyst neutralizer
UV Stabilizers	2-Hydroxy-4-octoxybenzophenone	Epoxy Resins Polyester (Terephthalate) Polyester (Alkyds) Polyethylene Low Density Linear Low Density High Density Polypropylene GP Polystyrene Impact Polystyrene ABS Polyvinyl Chloride Polyvinylidene Chloride	1. Low oral toxicity 2. FDA sanctioned for some food contact packaging 3. Powder 4. MP = 48-49°C 5. Used in conjunction with phenolic and thiodiopropionate antioxidants for polyolefins 6. Synergism with heat stabilizers in PVC 7. May tend to migrate in polyolefins 8. Typical concentrations: Polyolefins - 0.1-3.0%; PVC - 0.1-1.0%; Polyesters - 0.25-0.75%

(continued)

TABLE A-1 (continued)

Additive Class	Chemical	Polymer Application	Comments
UV Stabilizers (Cont.)	2(2'-Hydroxy-5'-methylphenyl)benzotriazole	Epoxy Resins Polyester (Terephthlate) Polyester (Alkyds) GP Polystyrene Impact Polystyrene ABS Polyvinyl Chloride Polyvinylidene Chloride	1. Oral toxicity low 2. FDA approved for some food contact packaging 3. Powder 4. MP = 192°C 5. Synergism with heat stabilizers in PVC 6. Acts both as a screening agent and as a quencher 7. May be too volatile for some applications. 8. Typical concentrations: PVC - 0.1-1.0%
	Nickel dibutyldithio carbamate	Polyethylene Low Density Linear Low Density High Density Polypropylene	1. Toxic 2. Flakes 3. MP = 88°C 4. Synergism with benzophenones and benzotriazoles 5. Reacts with sulfur in dilauryl thiodipropionate to form black nickel sulfide 6. Imparts olive-green color to the polymer
Urethane Catalysts	Triethylene diamine	Polyurethanes	1. Synergism with tin compounds
	Stannous octoate	Polyurethanes	1. Toxic 2. Remains in the foam, and may undergo hydrolysis of stannous to stannic 3. Synergism with amine catalysts
Plasticizers	Dioctyl phthalate (DOP)	Polyurethanes Polyvinyl Acetate Polyvinyl Alcohol Polyvinyl Chloride Polyvinylidene Chloride	1. Considered to be the industry standard 2. Approved for use as an adhesive by FDA 3. Approved for medical packaging by FDA (e.g., blood bags) 4. Available in masterbatches

(continued)

TABLE A-1 (continued)

Additive Class	Chemical	Polymer Application	Comments
Plasticizers (Cont'd)	Diisooctyl phthalate (DIOP)	Acrylics GP Polystyrene Impact Polystyrene Polyurethanes Polyvinyl Acetate (P) Polyvinyl Alcohol (P) Polyvinyl Chloride	
	Diisodecyl phthalate (DIDP)	Polyvinyl Chloride	1. Lower volatility than DOP 2. Lower plasticizing ability than DOP
	Tricresyl Phosphate	Acrylics (P) GP Polystyrene Impact Polystyrene Polyvinyl Acetate Polyvinyl Alcohol Polyvinyl Chloride Polyvinylidene Chloride	1. Toxic 2. Also acts as flame retardant 3. Offers maximum flame retardance among the phosphates but minimum plasticizing ability
	Di-(2-ethylhexyl)adipate	Acrylics (P) GP Polystyrene Impact Polystyrene Polyurethanes Polyvinyl Chloride Polyvinylidene Chloride	1. Good low temperature flexibility 2. Limited compatibility with resin 3. Approved for use in food packaging by FDA 4. Has relatively high volatility
Reinforcing Agents	Glass fibers	Acetals Amides Amino Resins Epoxy Resins Fluoroplastics Nylon 6 and 6/6 Phenolic Resins Polycarbonate Polyester (Terephthalate) Polyester (Alkyds) High Density Polyethylene Polyphenylene Oxide Polyphenylene Sulfide Polypropylene Impact Polystyrene ABS SAN	1. Various strengths available 2. Easily damaged during extrusion 3. Available as ribbons, yarns, fabrics, rovings, mats, filaments or chopped strands

(continued)

TABLE A-1 (continued)

Additive Class	Chemical	Polymer Application	Comments
Reinforcing Agents (Cont'd)	Asbestos Serpentine Amphibole Amosite	Acetals Amides Amino Resins Epoxy Resins Fluoroplastics Nylon 6 and 6/6 Phenolic Resins Polycarbonate Polyester (Terephthalate) Polyester (Alkyds) Polyethylene Low Density Linear Low Density High Density Polyphenylene Oxide Polypropylene Impact Polystyrene Polyvinyl Chloride	1. Toxic 2. Carcinogenic 3. Extruders have vacuum vent for densification 4. Pelletized forms available
	Silica Quartz Diatomaceous Silica Synthetic Novaculite	Acetals Acrylics Amino Resins Epoxy Resins Nylon 6 and 6/6 Phenolic Resins Polycarbonate Polyester (Alkyds) Polyethylene Low Density Linear Low Density Polyphenylene Oxide Polyphenylene Sulfide Polyvinyl Acetate Polyvinyl Alcohol Polyvinyl Chloride	1. Abrasive 2. Prolong exposure causes lung damage (silicosis) 3. Also acts as a filler 4. Fumed silica or diatomaceous earth may be used as an anti-blocking agent for polyolefin films or as a viscosity modifier for polyvinyl chloride coatings 5. Quartz used in epoxy and phenolic resins for high-performance aerospace applications

(continued)

TABLE A-1 (continued)

C = Coated Lead Chromate
P = Partially Compatible

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APPENDIX B. POLYMER PROCESS PRODUCT DIAGRAMS FOR THE PLASTICS AND RESINS PROCESSING INDUSTRY

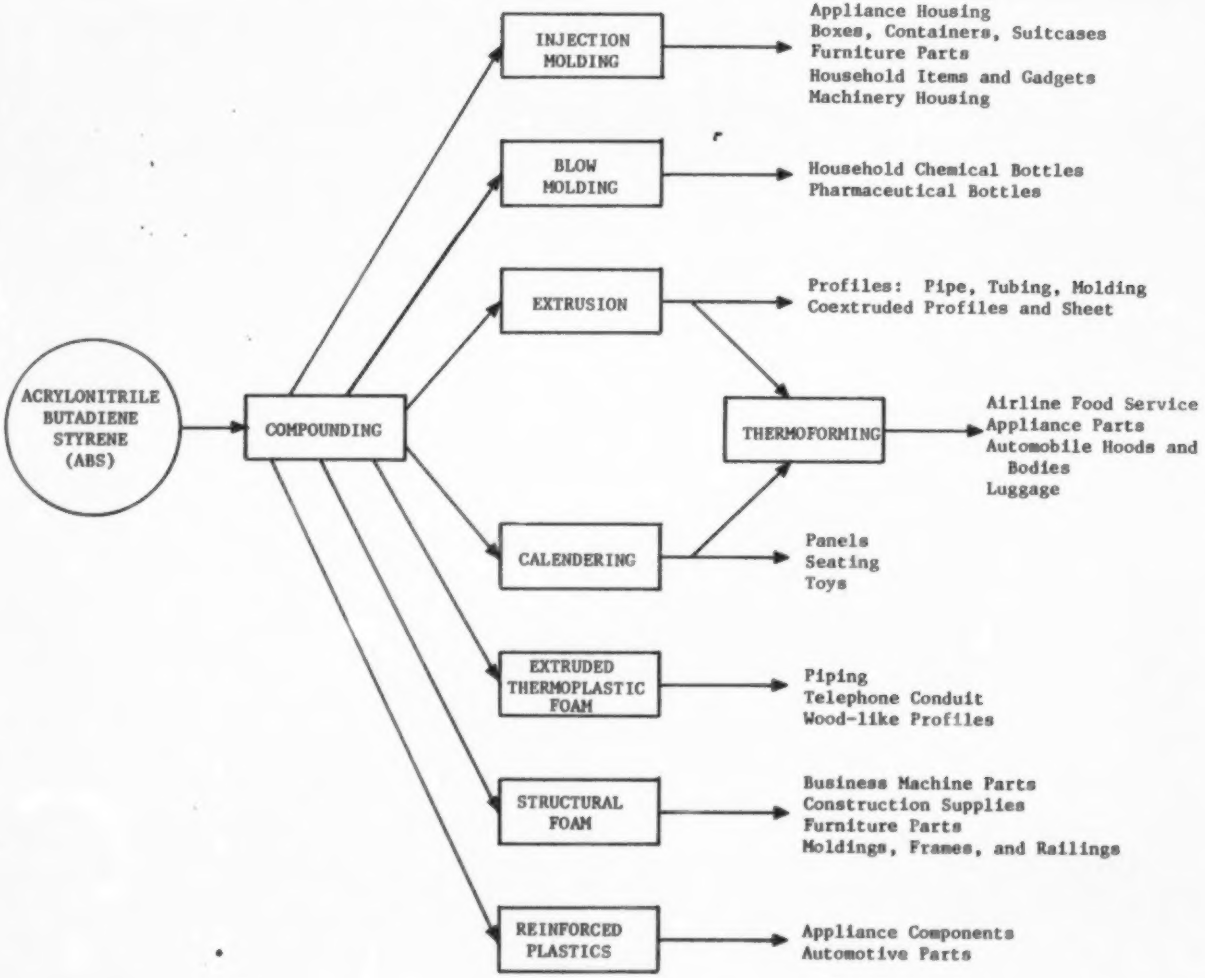

ACRYLONITRILE
BUTADIENE
STYRENE
(ABS)
COMPOUNDING
INJECTION MOLDING
BLOW MOLDING
EXTRUSION
CALENDERING
EXTRUDED THERMOPLASTIC FOAM
STRUCTURAL FOAM
REINFORCED PLASTICS
THERMOFORMING
Appliance Housing
Boxes, Containers, Suitcases
Furniture Parts
Household Items and Gadgets
Machinery Housing
Household Chemical Bottles
Pharmaceutical Bottles
Profiles: Pipe, Tubing, Molding
Coextruded Profiles and Sheet
Airline Food Service
Appliance Parts
Automobile Hoods and Bodies
Luggage
Panels
Seating
Toys
Piping
Telephone Conduit
Wood-like Profiles
Business Machine Parts
Construction Supplies
Furniture Parts
Moldings, Frames, and Railings
Appliance Components
Automotive Parts

Figure B-1. Polymer-process-product (PPP) link.

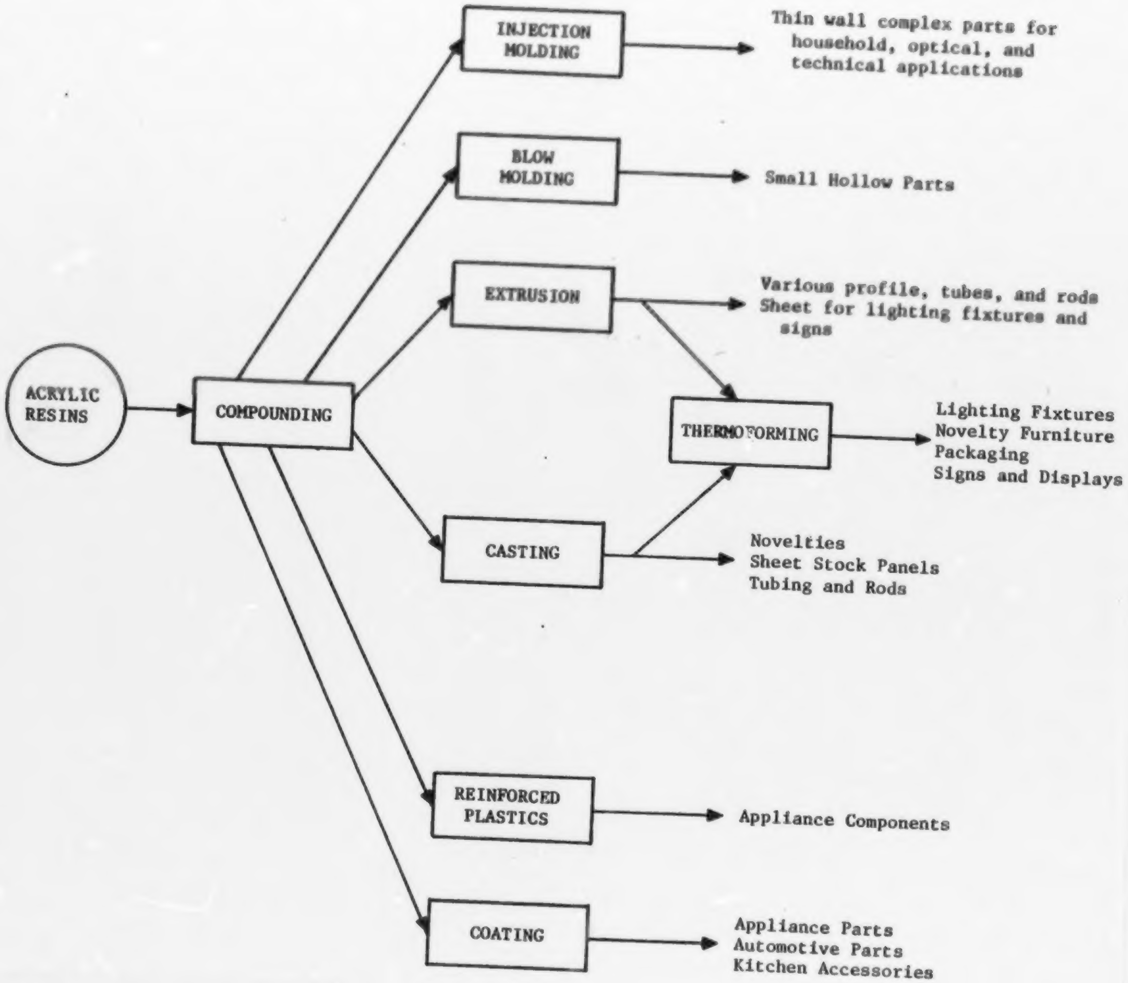

ACRYLIC RESINS
COMPOUNDING
INJECTION MOLDING
BLOW MOLDING
EXTRUSION
THERMOFORMING
CASTING
REINFORCED PLASTICS
COATING
Thin wall complex parts for household, optical, and technical applications
Small Hollow Parts
Various profile, tubes, and rods
Sheet for lighting fixtures and signs
Lighting Fixtures
Novelty Furniture
Packaging
Signs and Displays
Novelties
Sheet Stock Panels
Tubing and Rods
Appliance Components
Appliance Parts
Automotive Parts
Kitchen Accessories

Figure B-1 (continued)

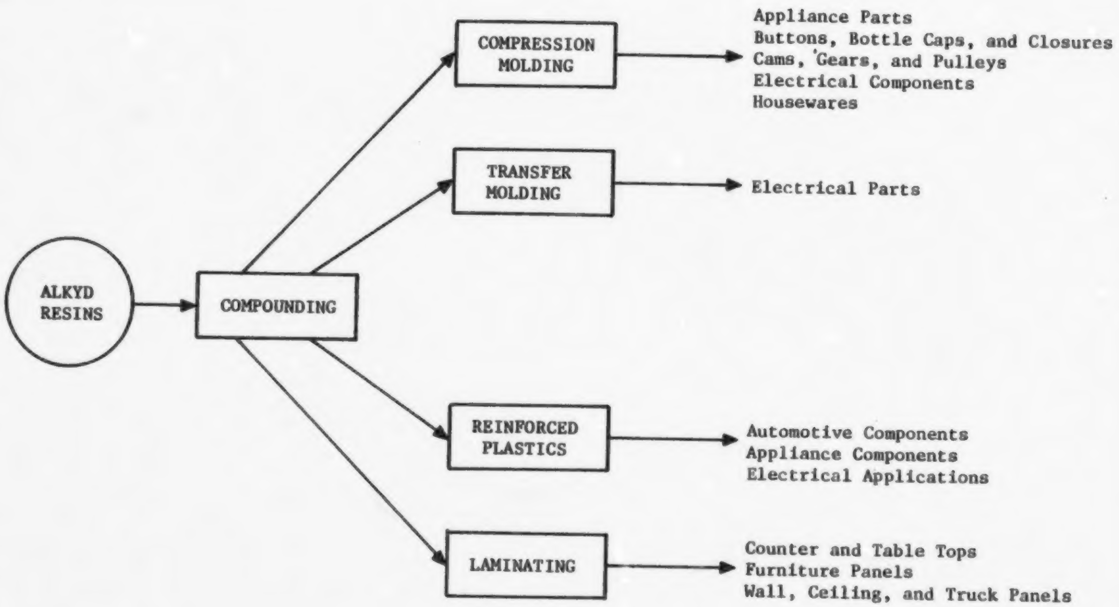

ALKYD RESINS
COMPOUNDING
COMPRESSION MOLDING
Appliance Parts
Buttons, Bottle Caps, and Closures
Cams, Gears, and Pulleys
Electrical Components
Housewares
TRANSFER MOLDING
Electrical Parts
REINFORCED PLASTICS
Automotive Components
Appliance Components
Electrical Applications
LAMINATING
Counter and Table Tops
Furniture Panels
Wall, Ceiling, and Truck Panels

Figure B-1 (continued)

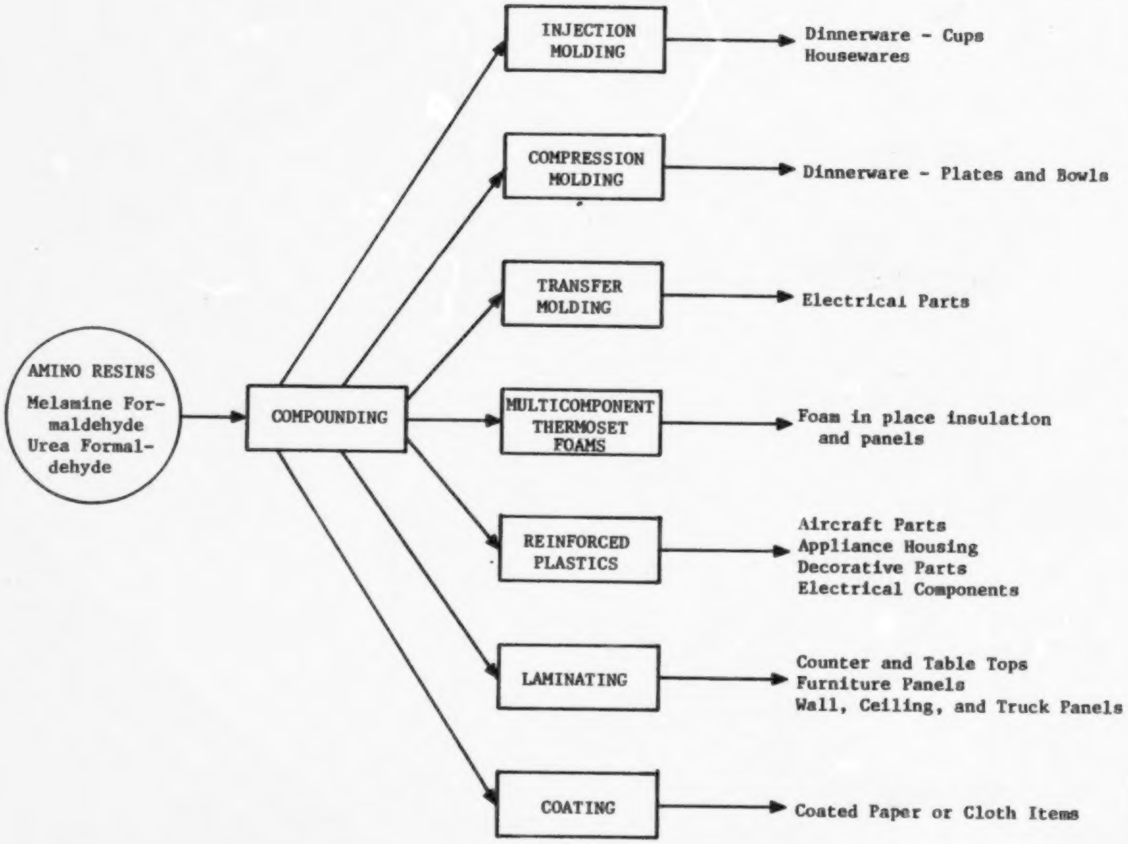
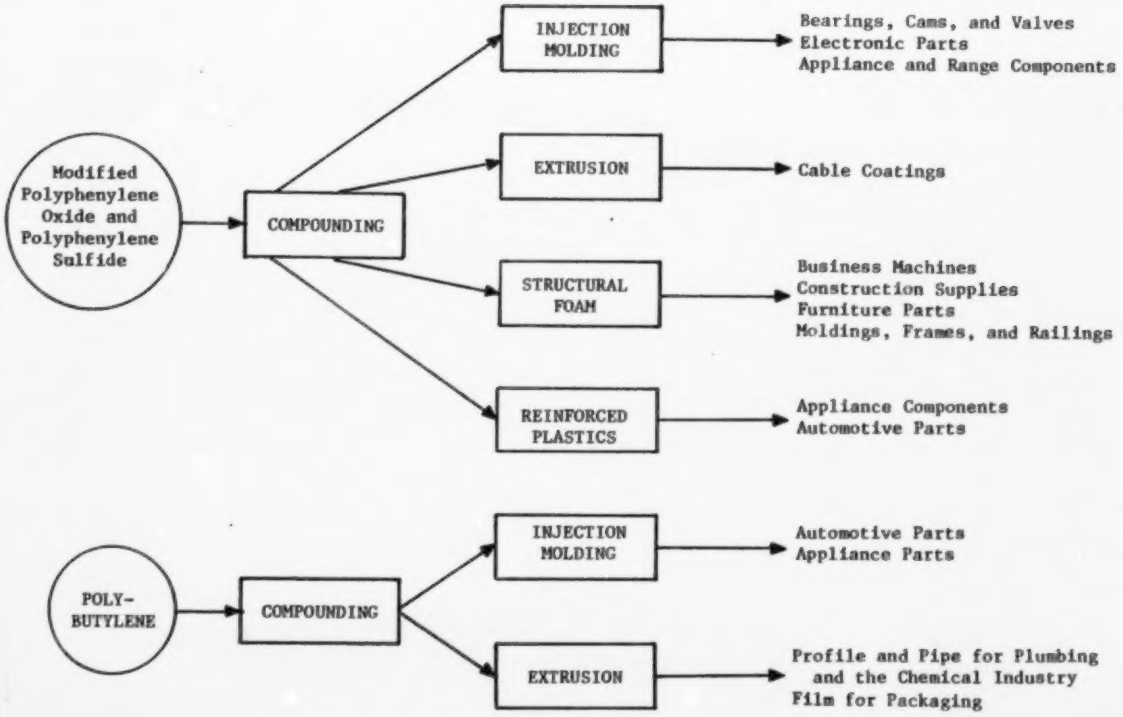

AMINO RESINS
Melamine Formaldehyde
Urea Formaldehyde
COMPOUNDING
INJECTION MOLDING
COMPRESSION MOLDING
TRANSFER MOLDING
MULTICOMPONENT THERMOSET FOAMS
REINFORCED PLASTICS
LAMINATING
COATING
Dinnerware - Cups
Housewares
Dinnerware - Plates and Bowls
Electrical Parts
Foam in place insulation and panels
Aircraft Parts
Appliance Housing
Decorative Parts
Electrical Components
Counter and Table Tops
Furniture Panels
Wall, Ceiling, and Truck Panels
Coated Paper or Cloth Items

Figure B-1 (continued)


Modified Polyphenylene Oxide and Polyphenylene Sulfide
COMPOUNDING
INJECTION MOLDING
Bearings, Cams, and Valves
Electronic Parts
Appliance and Range Components
EXTRUSION
Cable Coatings
STRUCTURAL FOAM
Business Machines
Construction Supplies
Furniture Parts
Moldings, Frames, and Railings
REINFORCED PLASTICS
Appliance Components
Automotive Parts
POLY-BUTYLENE
COMPOUNDING
INJECTION MOLDING
Automotive Parts
Appliance Parts
EXTRUSION
Profile and Pipe for Plumbing and the Chemical Industry
Film for Packaging

Appendix B-1 (continued)

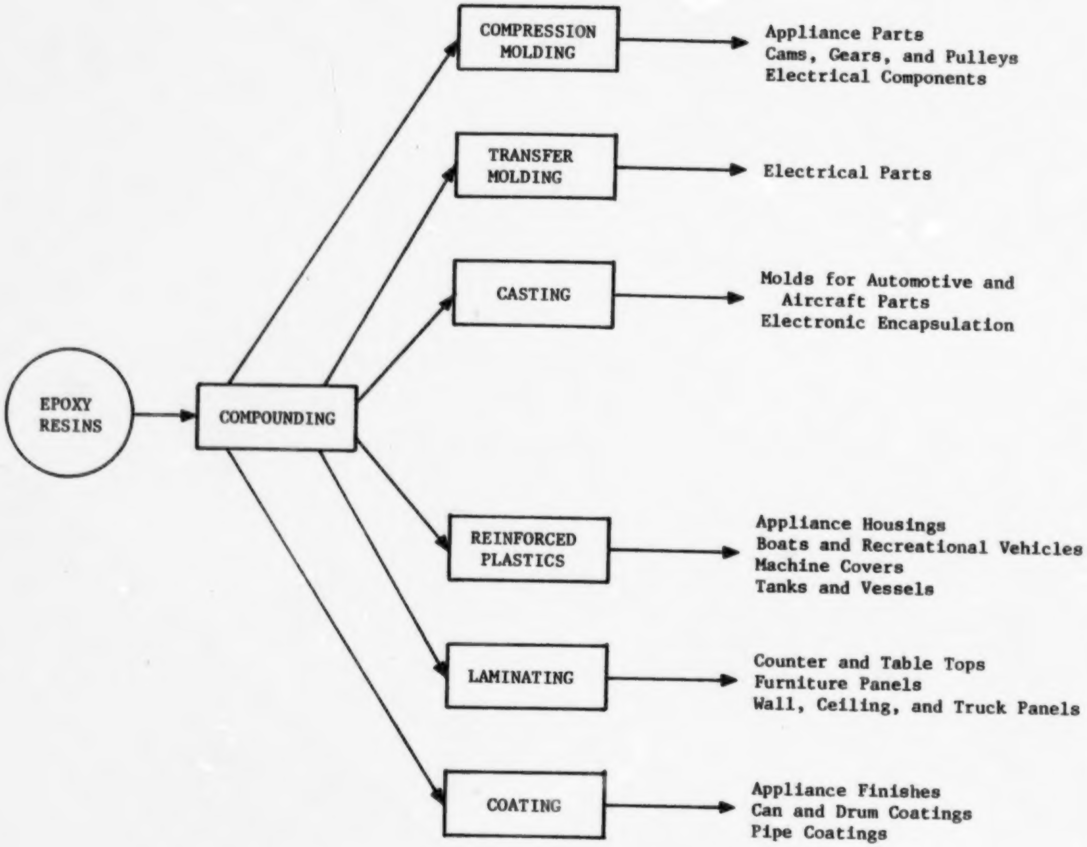

EPOXY RESINS
COMPOUNDING
COMPRESSION MOLDING
TRANSFER MOLDING
CASTING
REINFORCED PLASTICS
LAMINATING
COATING
Appliance Parts
Cams, Gears, and Pulleys
Electrical Components
Electrical Parts
Molds for Automotive and Aircraft Parts
Electronic Encapsulation
Appliance Housings
Boats and Recreational Vehicles
Machine Covers
Tanks and Vessels
Counter and Table Tops
Furniture Panels
Wall, Ceiling, and Truck Panels
Appliance Finishes
Can and Drum Coatings
Pipe Coatings

Figure B-1 (continued)

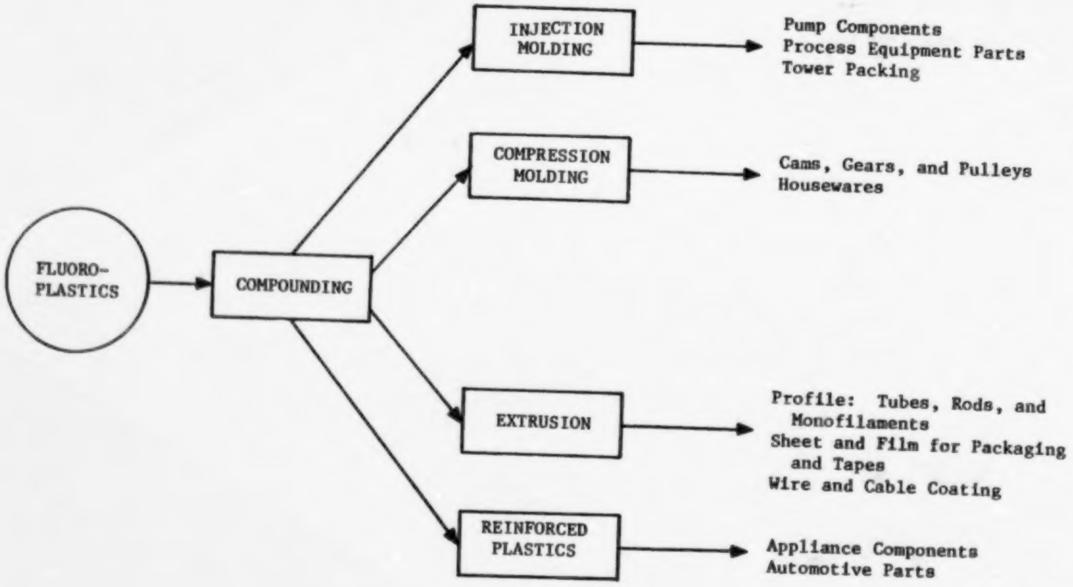

FLUORO-
PLASTICS
COMPOUNDING
INJECTION MOLDING
COMPRESSION MOLDING
EXTRUSION
REINFORCED PLASTICS
Pump Components
Process Equipment Parts
Tower Packing
Cams, Gears, and Pulleys
Housewares
Profile: Tubes, Rods, and Monofilaments
Sheet and Film for Packaging and Tapes
Wire and Cable Coating
Appliance Components
Automotive Parts

Figure B-1 (continued)

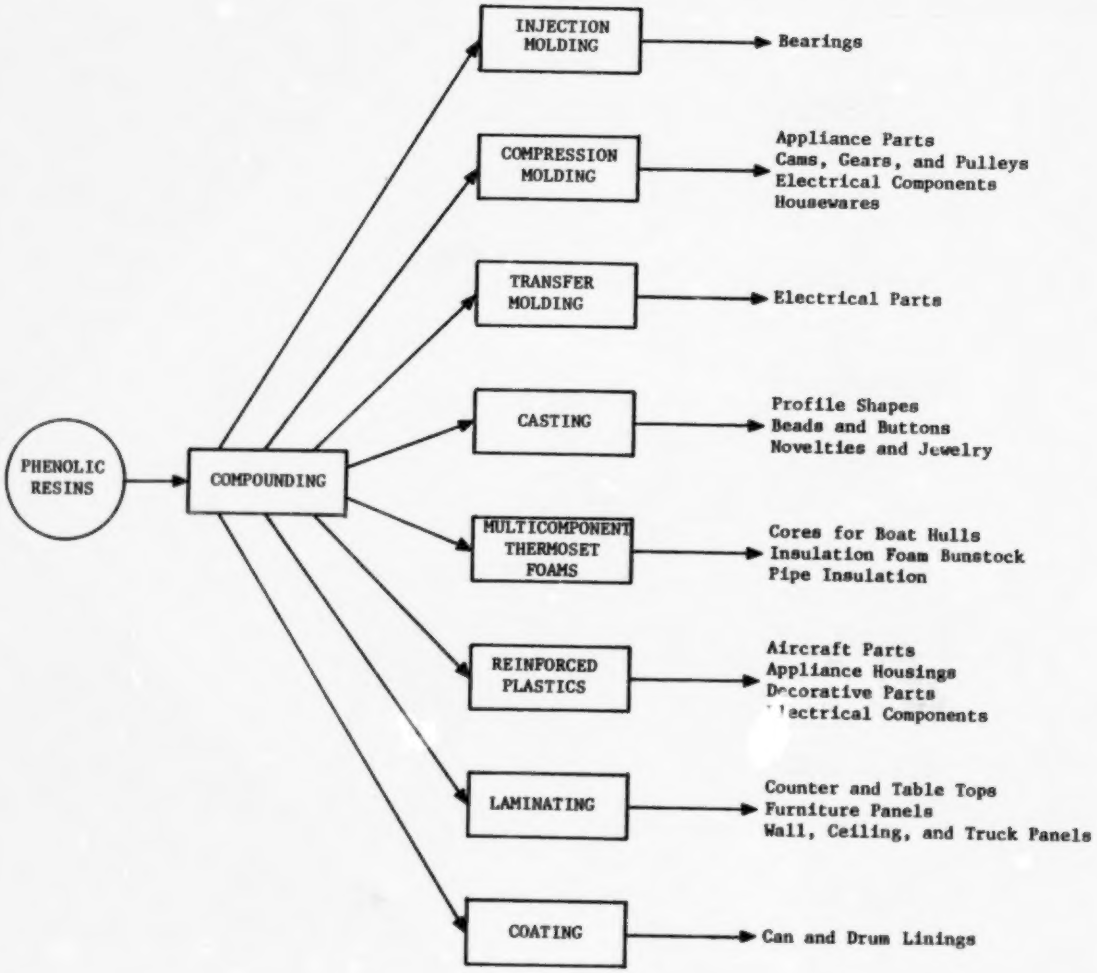

PHENOLIC RESINS
COMPOUNDING
INJECTION MOLDING
Bearings
COMPRESSION MOLDING
Appliance Parts
Cams, Gears, and Pulleys
Electrical Components
Housewares
TRANSFER MOLDING
Electrical Parts
CASTING
Profile Shapes
Beads and Buttons
Novelties and Jewelry
MULTICOMPONENT THERMOSET FOAMS
Cores for Boat Hulls
Insulation Foam Bunstock
Pipe Insulation
REINFORCED PLASTICS
Aircraft Parts
Appliance Housings
Decorative Parts
Electrical Components
LAMINATING
Counter and Table Tops
Furniture Panels
Wall, Ceiling, and Truck Panels
COATING
Can and Drum Linings

Figure B-1 (continued)

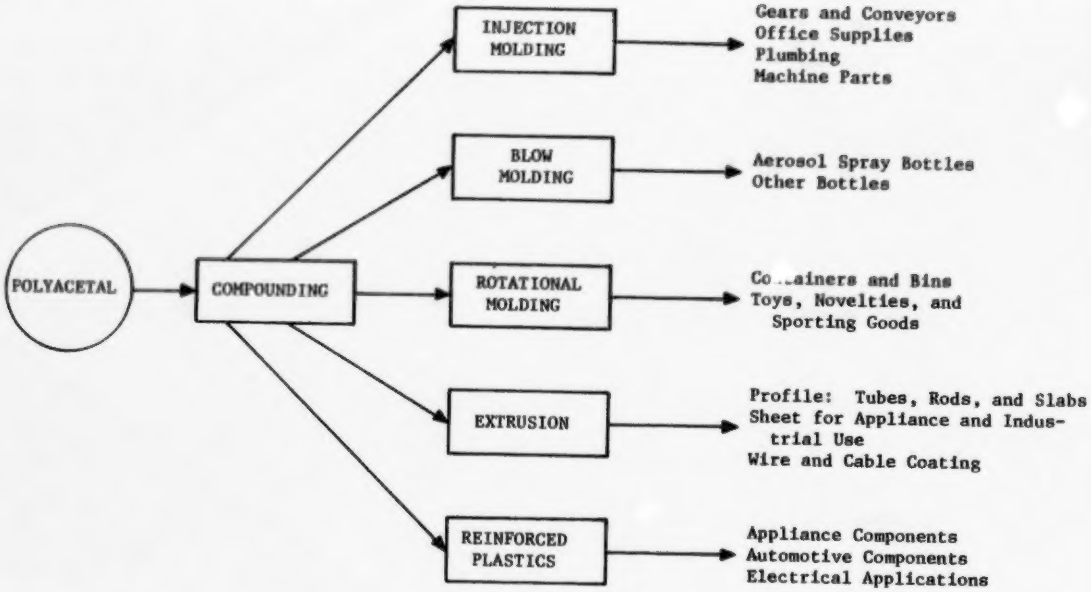

POLYACETAL
COMPOUNDING
INJECTION MOLDING
BLOW MOLDING
ROTATIONAL MOLDING
EXTRUSION
REINFORCED PLASTICS
Gears and Conveyors
Office Supplies
Plumbing
Machine Parts
Aerosol Spray Bottles
Other Bottles
Containers and Bins
Toys, Novelties, and Sporting Goods
Profile: Tubes, Rods, and Slabs
Sheet for Appliance and Industrial Use
Wire and Cable Coating
Appliance Components
Automotive Components
Electrical Applications

Figure B-1 (continued)

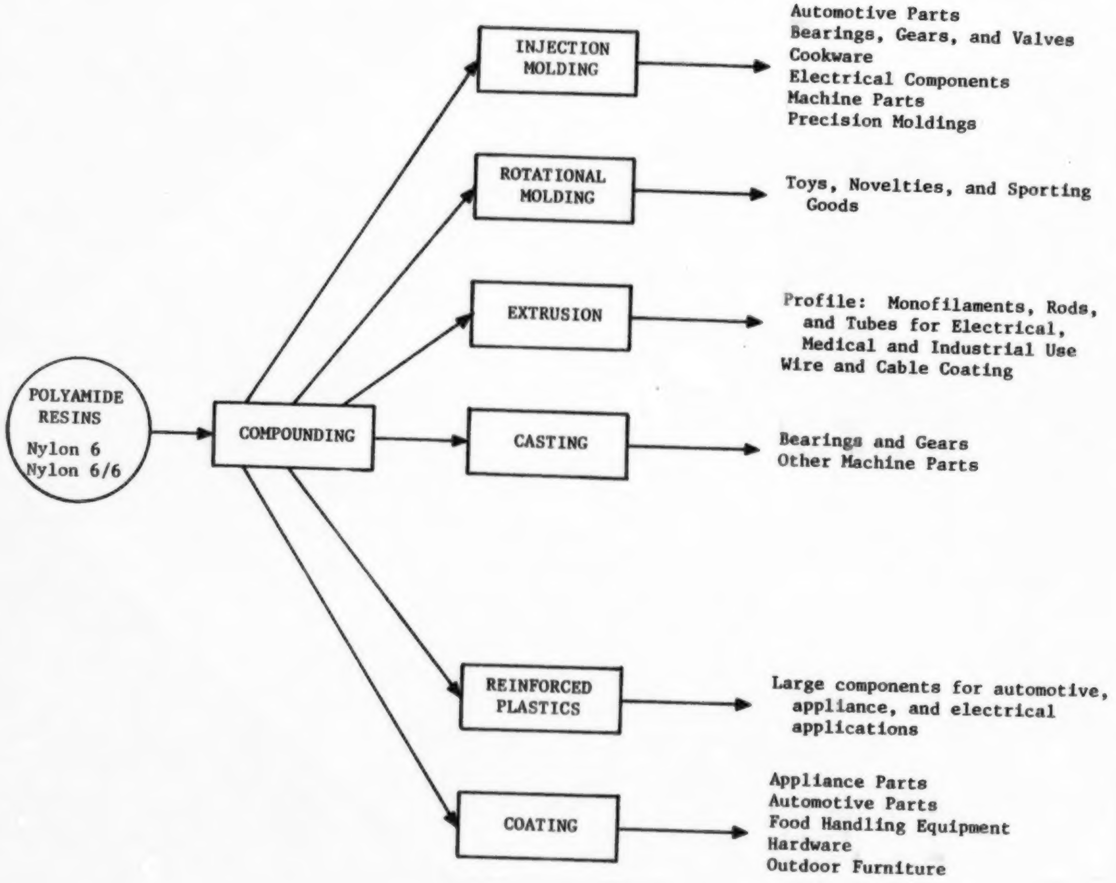

POLYAMIDE RESINS
Nylon 6
Nylon 6/6
COMPOUNDING
INJECTION MOLDING
ROTATIONAL MOLDING
EXTRUSION
CASTING
REINFORCED PLASTICS
COATING
Automotive Parts
Bearings, Gears, and Valves
Cookware
Electrical Components
Machine Parts
Precision Moldings
Toys, Novelties, and Sporting Goods
Profile: Monofilaments, Rods, and Tubes for Electrical, Medical and Industrial Use
Wire and Cable Coating
Bearings and Gears
Other Machine Parts
Large components for automotive, appliance, and electrical applications
Appliance Parts
Automotive Parts
Food Handling Equipment
Hardware
Outdoor Furniture

Figure B-1 (continued)

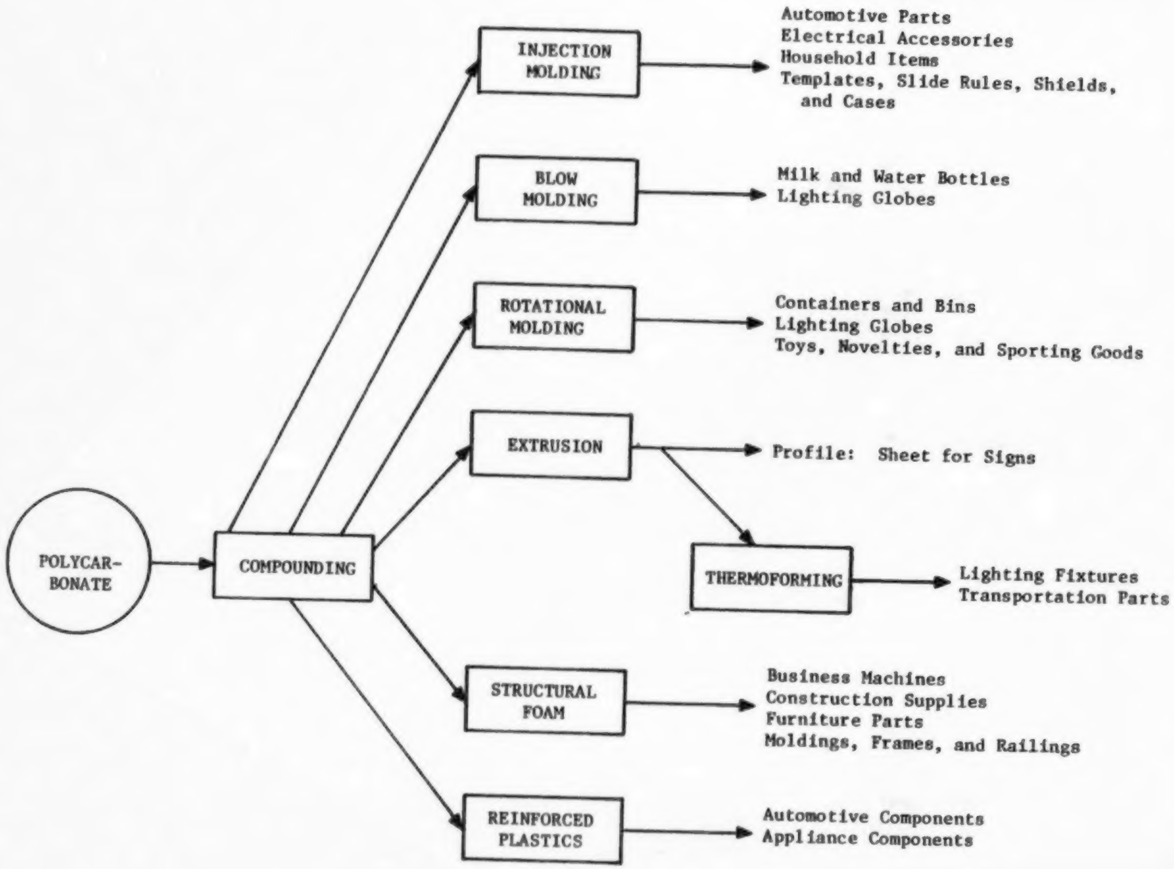

POLYCAR-
BONATE
COMPOUNDING
INJECTION MOLDING
Automotive Parts
Electrical Accessories
Household Items
Templates, Slide Rules, Shields, and Cases
BLOW MOLDING
Milk and Water Bottles
Lighting Globes
ROTATIONAL MOLDING
Containers and Bins
Lighting Globes
Toys, Novelties, and Sporting Goods
EXTRUSION
Profile: Sheet for Signs
THERMOFORMING
Lighting Fixtures
Transportation Parts
STRUCTURAL FOAM
Business Machines
Construction Supplies
Furniture Parts
Moldings, Frames, and Railings
REINFORCED PLASTICS
Automotive Components
Appliance Components

Figure B-1 (continued)

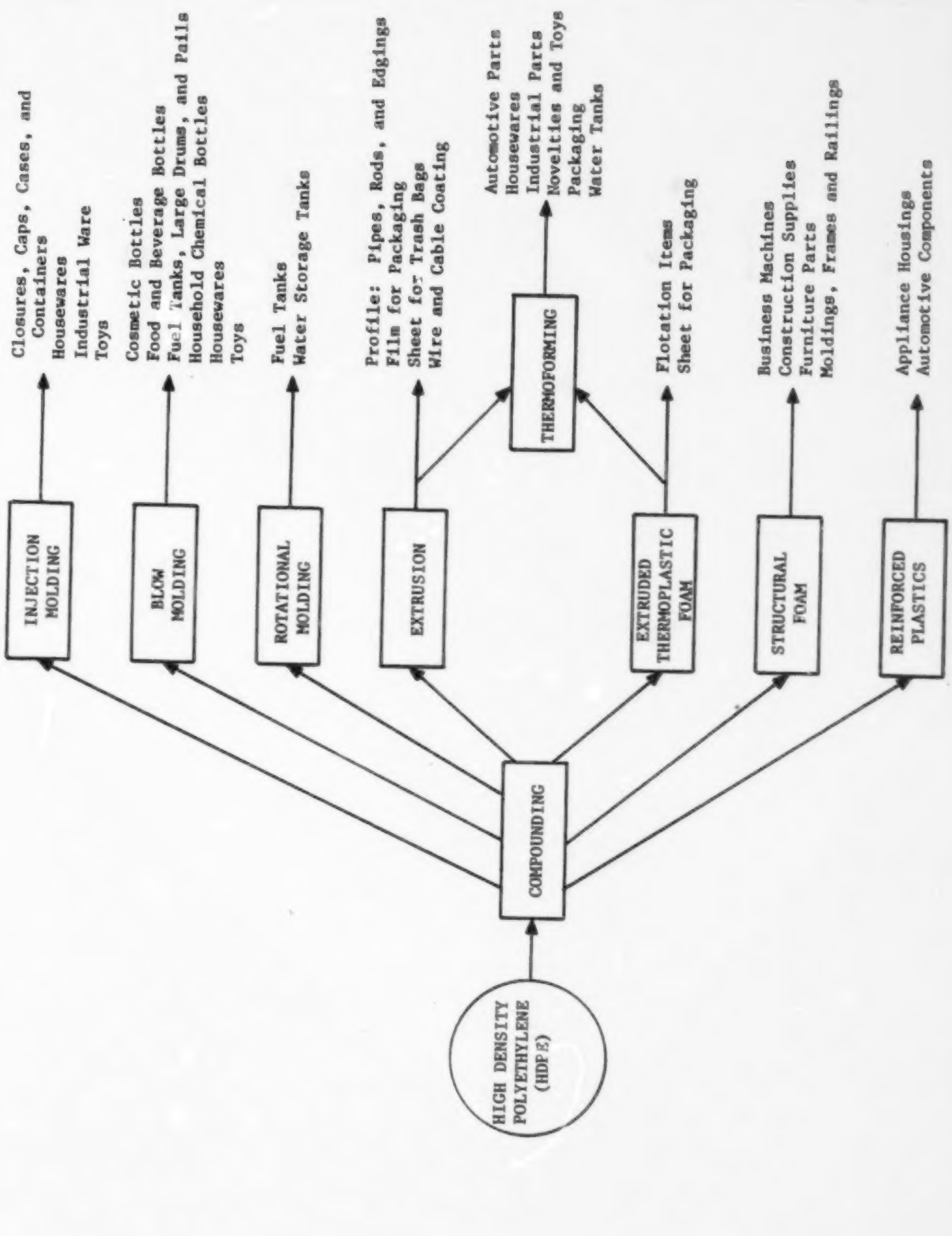

HIGH DENSITY POLYETHYLENE (HDPE)
COMPOUNDING
INJECTION MOLDING
Closures, Caps, Cases, and Containers
Housewares
Industrial Ware
Toys
BLOW MOLDING
Cosmetic Bottles
Food and Beverage Bottles
Fuel Tanks, Large Drums, and Pails
Household Chemical Bottles
Housewares
Toys
ROTATIONAL MOLDING
Fuel Tanks
Water Storage Tanks
EXTRUSION
Profile: Pipes, Rods, and Edgings
Film for Packaging
Sheet for Trash Bags
Wire and Cable Coating
THERMOFORMING
Automotive Parts
Housewares
Industrial Parts
Novelties and Toys
Packaging
Water Tanks
EXTRUDED THERMOPLASTIC FOAM
Flotation Items
Sheet for Packaging
STRUCTURAL FOAM
Business Machines
Construction Supplies
Furniture Parts
Moldings, Frames and Railings
REINFORCED PLASTICS
Appliance Housings
Automotive Components

Figure B-1 (continued)

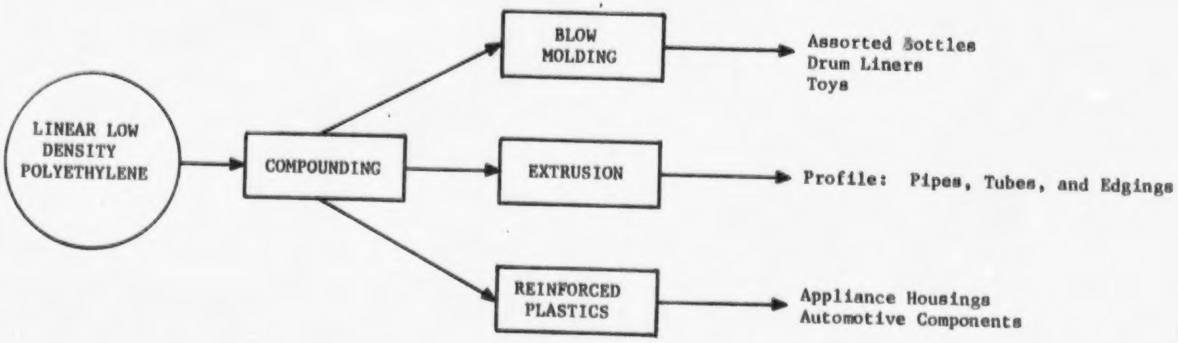

LINEAR LOW DENSITY POLYETHYLENE
COMPOUNDING
BLOW MOLDING
EXTRUSION
REINFORCED PLASTICS
Assorted Bottles
Drum Liners
Toys
Profile: Pipes, Tubes, and Edgings
Appliance Housings
Automotive Components

Figure B-1 (continued)

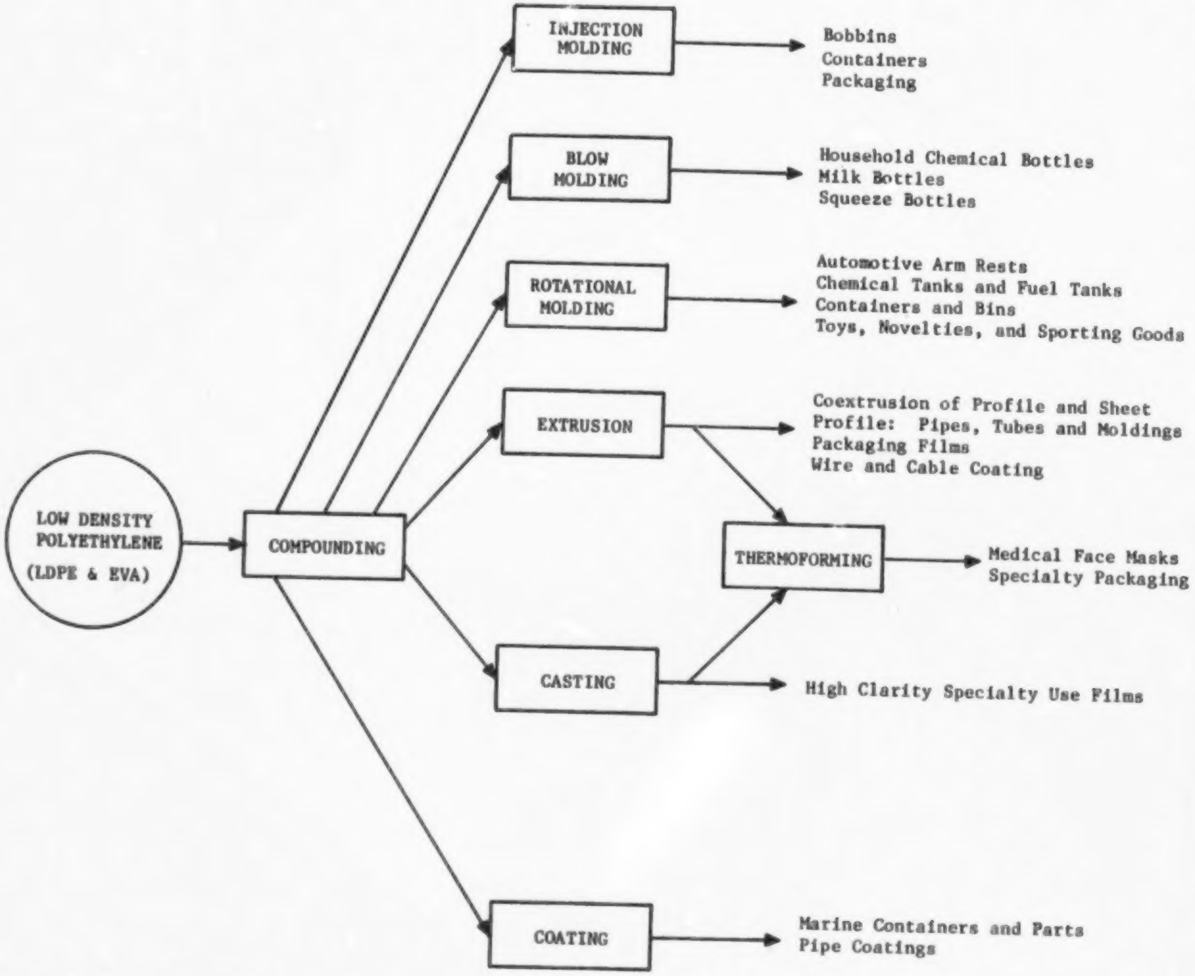

LOW DENSITY POLYETHYLENE (LDPE & EVA)
COMPOUNDING
INJECTION MOLDING
Bobbins
Containers
Packaging
BLOW MOLDING
Household Chemical Bottles
Milk Bottles
Squeeze Bottles
ROTATIONAL MOLDING
Automotive Arm Rests
Chemical Tanks and Fuel Tanks
Containers and Bins
Toys, Novelties, and Sporting Goods
EXTRUSION
Coextrusion of Profile and Sheet
Profile: Pipes, Tubes and Moldings
Packaging Films
Wire and Cable Coating
THERMOFORMING
Medical Face Masks
Specialty Packaging
CASTING
High Clarity Specialty Use Films
COATING
Marine Containers and Parts
Pipe Coatings

Figure B-1 (continued)

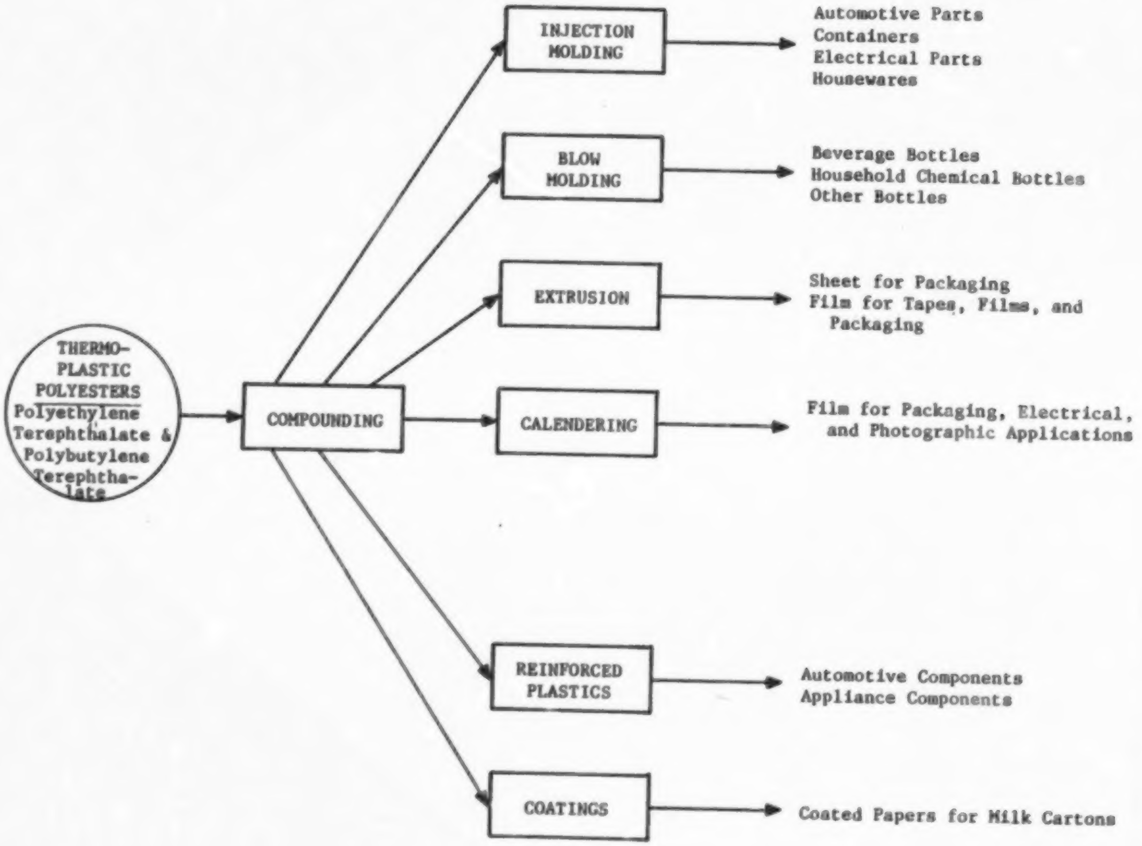

THERMO-
PLASTIC
POLYESTERS
Polyethylene
Terephthalate &
Polybutylene
Terephthalate
COMPOUNDING
INJECTION MOLDING
BLOW MOLDING
EXTRUSION
CALENDERING
REINFORCED PLASTICS
COATINGS
Automotive Parts
Containers
Electrical Parts
Housewares
Beverage Bottles
Household Chemical Bottles
Other Bottles
Sheet for Packaging
Film for Tapes, Films, and Packaging
Film for Packaging, Electrical, and Photographic Applications
Automotive Components
Appliance Components
Coated Papers for Milk Cartons

Figure B-1 (continued)

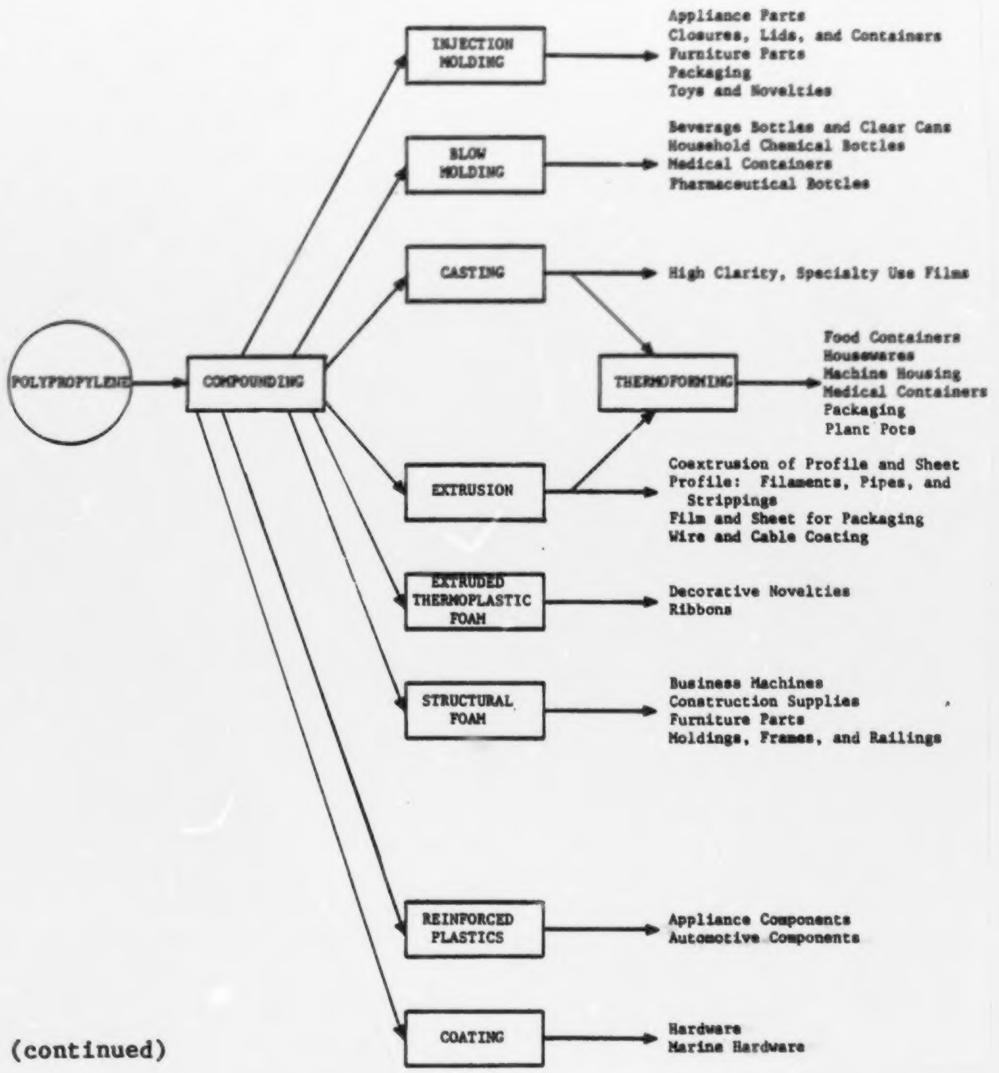

POLYPROPYLENE
COMPOUNDING
INJECTION MOLDING
Appliance Parts
Closures, Lids, and Containers
Furniture Parts
Packaging
Toys and Novelties
BLOW MOLDING
Beverage Bottles and Clear Cans
Household Chemical Bottles
Medical Containers
Pharmaceutical Bottles
CASTING
High Clarity, Specialty Use Films
THERMOFORMING
Food Containers
Housewares
Machine Housing
Medical Containers
Packaging
Plant Pots
EXTRUSION
Coextrusion of Profile and Sheet
Profile: Filaments, Pipes, and Strippings
Film and Sheet for Packaging
Wire and Cable Coating
EXTRUDED THERMOPLASTIC FOAM
Decorative Novelties
Ribbons
STRUCTURAL FOAM
Business Machines
Construction Supplies
Furniture Parts
Moldings, Frames, and Railings
REINFORCED PLASTICS
Appliance Components
Automotive Components
COATING
Hardware
Marine Hardware

Figure B-1 (continued)

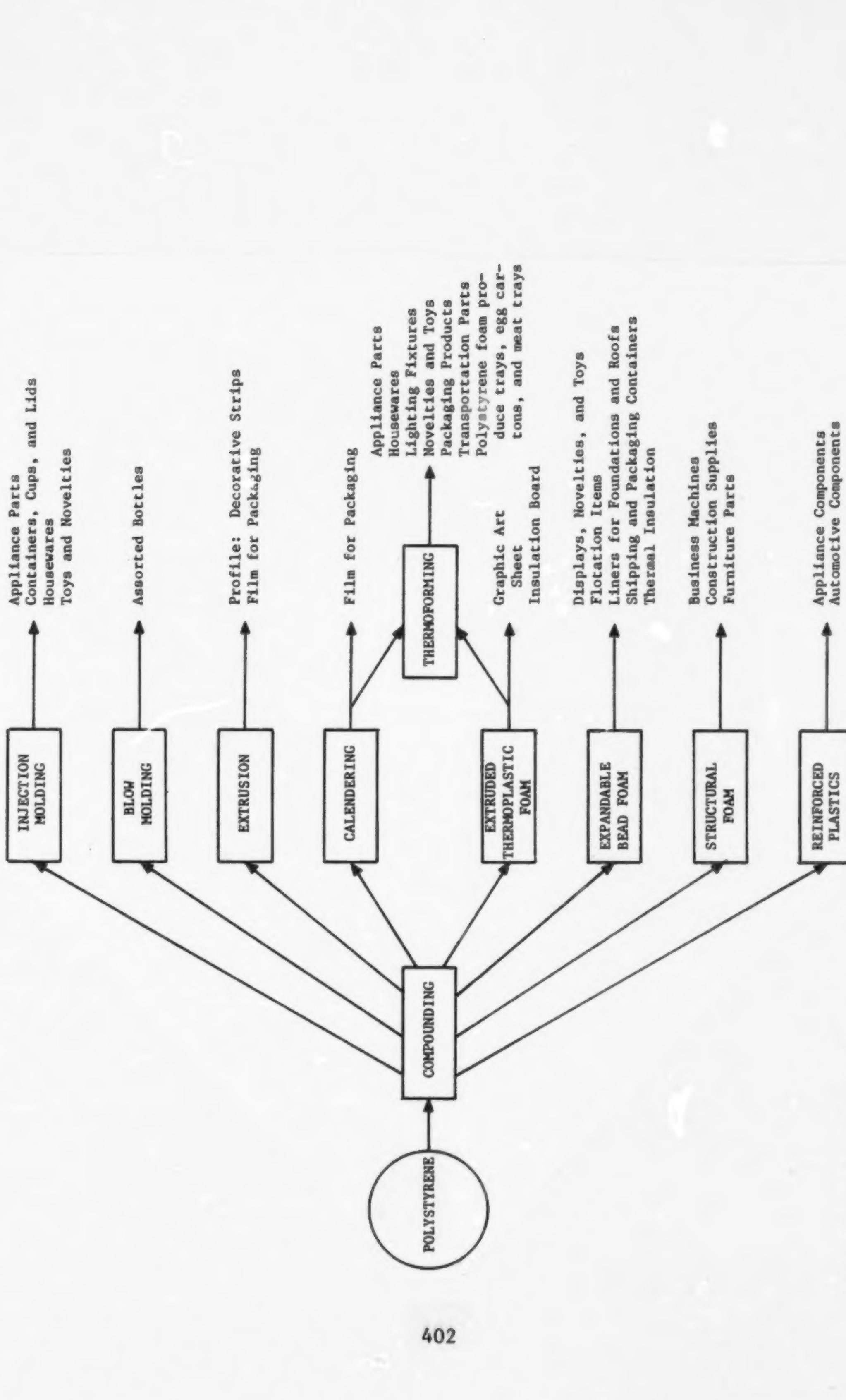

POLYSTYRENE
COMPOUNDING
INJECTION MOLDING
Appliance Parts
Containers, Cups, and Lids
Housewares
Toys and Novelties
BLOW MOLDING
Assorted Bottles
EXTRUSION
Profile: Decorative Strips
Film for Packaging
CALENDERING
Film for Packaging
THERMOFORMING
Appliance Parts
Housewares
Lighting Fixtures
Novelties and Toys
Packaging Products
Transportation Parts
Polystyrene foam produce trays, egg cartons, and meat trays
EXTRUDED THERMOPLASTIC FOAM
Graphic Art Sheet
Insulation Board
EXPANDABLE BEAD FOAM
Displays, Novelties, and Toys
Flotation Items
Liners for Foundations and Roofs
Shipping and Packaging Containers
Thermal Insulation
STRUCTURAL FOAM
Business Machines
Construction Supplies
Furniture Parts
REINFORCED PLASTICS
Appliance Components
Automotive Components

Figure B-1 (continued)

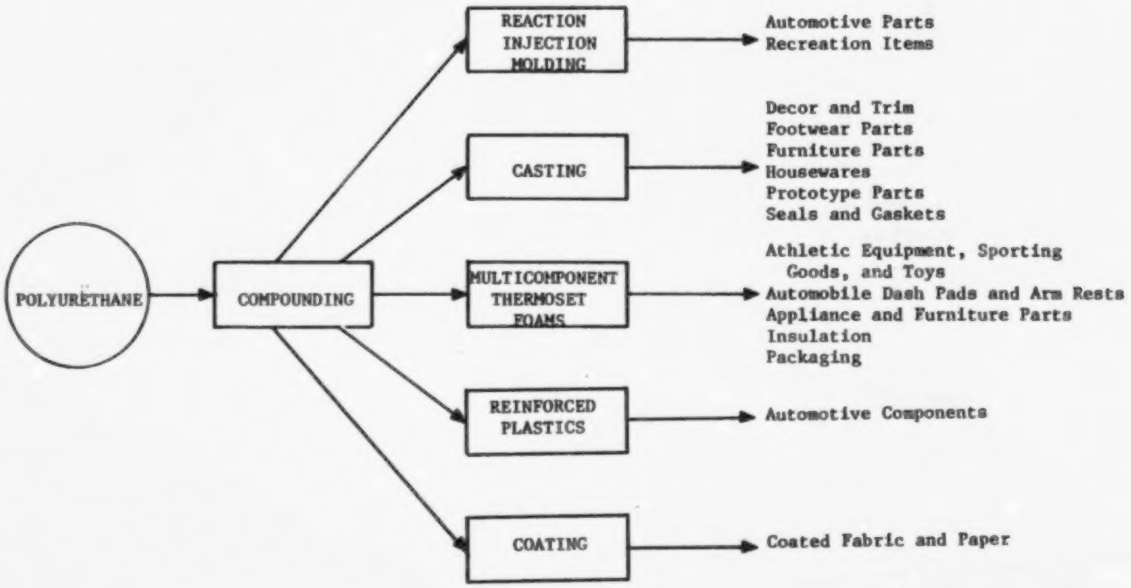

POLYURETHANE
COMPOUNDING
REACTION INJECTION MOLDING
CASTING
MULTICOMPONENT THERMOSET FOAMS
REINFORCED PLASTICS
COATING
Automotive Parts
Recreation Items
Decor and Trim
Footwear Parts
Furniture Parts
Housewares
Prototype Parts
Seals and Gaskets
Athletic Equipment, Sporting Goods, and Toys
Automobile Dash Pads and Arm Rests
Appliance and Furniture Parts
Insulation
Packaging
Automotive Components
Coated Fabric and Paper

Figure B-1 (continued)

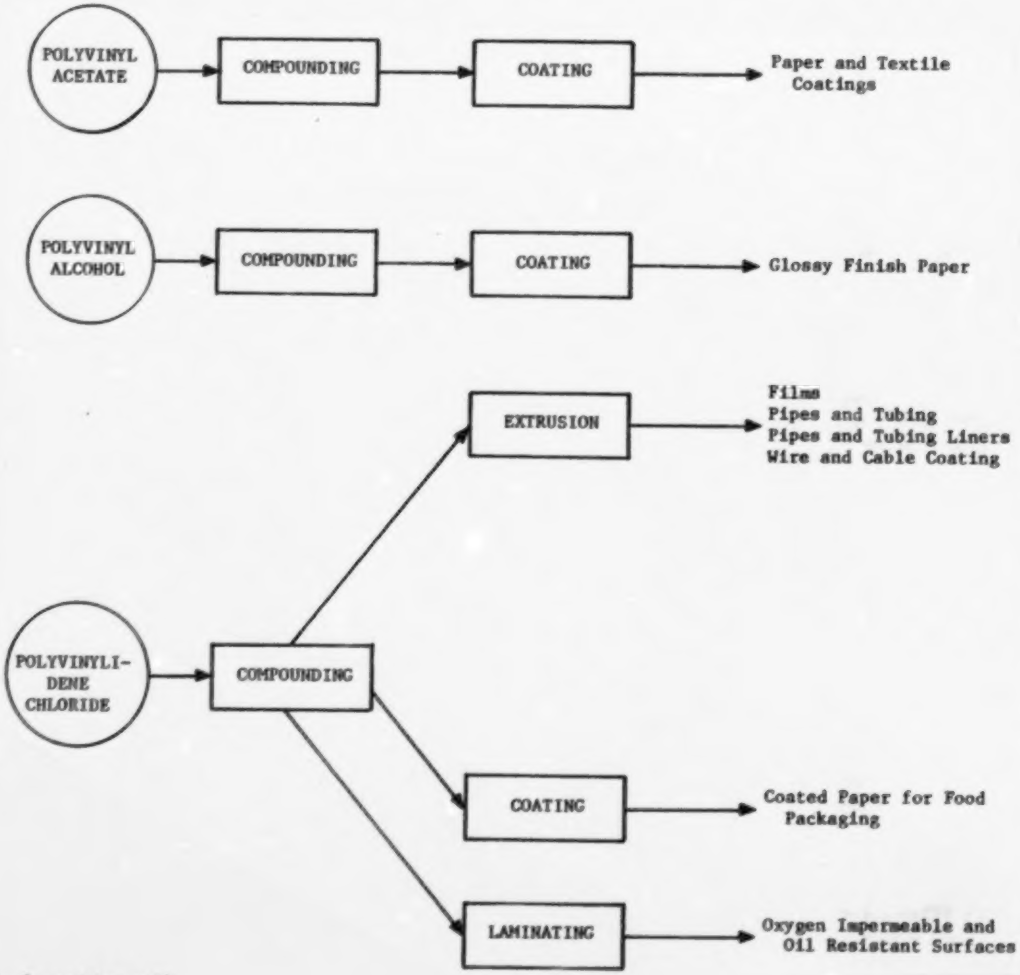

POLYVINYL ACETATE
COMPOUNDING
COATING
Paper and Textile Coatings
POLYVINYL ALCOHOL
COMPOUNDING
COATING
Glossy Finish Paper
POLYVINYLI-DENE CHLORIDE
COMPOUNDING
EXTRUSION
Films
Pipes and Tubing
Pipes and Tubing Liners
Wire and Cable Coating
COATING
Coated Paper for Food Packaging
LAMINATING
Oxygen Impermeable and Oil Resistant Surfaces

Figure B-1 (continued)

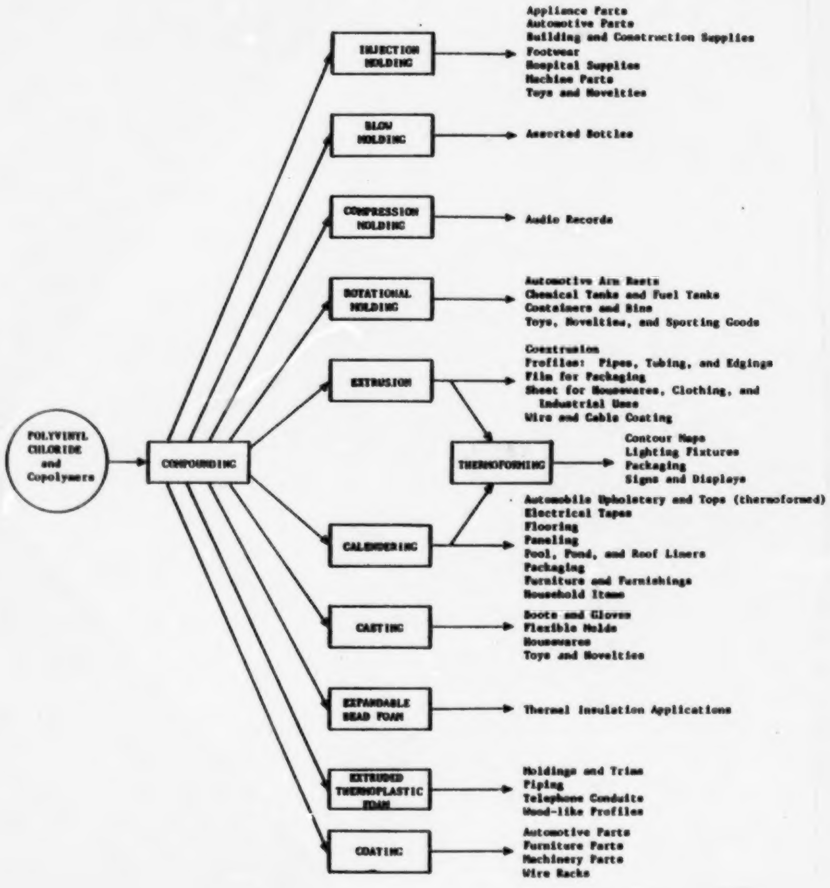

POLYVINYL CHLORIDE and Copolymers
COMPOUNDING
INJECTION MOLDING
Appliance Parts
Automotive Parts
Building and Construction Supplies
Footwear
Hospital Supplies
Machine Parts
Toys and Novelties
BLOW MOLDING
Assorted Bottles
COMPRESSION MOLDING
Audio Records
ROTATIONAL MOLDING
Automotive Arm Rests
Chemical Tanks and Fuel Tanks
Containers and Bins
Toys, Novelties, and Sporting Goods
EXTRUSION
Coextrusion
Profiles: Pipes, Tubing, and Edgings
Film for Packaging
Sheet for Housewares, Clothing, and Industrial Uses
Wire and Cable Coating
THERMOFORMING
Contour Maps
Lighting Fixtures
Packaging
Signs and Displays
CALENDERING
Automobile Upholstery and Tops (thermoformed)
Electrical Tapes
Flooring
Paneling
Pool, Pond, and Roof Liners
Packaging
Furniture and Furnishings
Household Items
CASTING
Boots and Gloves
Flexible Molds
Housewares
Toys and Novelties
EXPANDABLE BEAD FOAM
Thermal Insulation Applications
EXTRUDED THERMOPLASTIC FOAM
Moldings and Trims
Piping
Telephone Conduits
Wood-like Profiles
COATING
Automotive Parts
Furniture Parts
Machinery Parts
Wire Racks

Figure B-1 (continued)

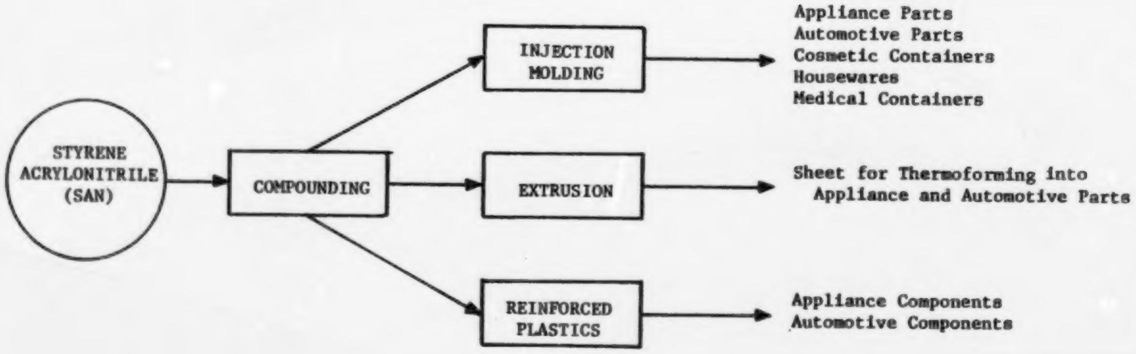

STYRENE ACRYLONITRILE (SAN)
COMPOUNDING
INJECTION MOLDING
EXTRUSION
REINFORCED PLASTICS
Appliance Parts
Automotive Parts
Cosmetic Containers
Housewares
Medical Containers
Sheet for Thermoforming into Appliance and Automotive Parts
Appliance Components
Automotive Components

Figure B-1 (continued)

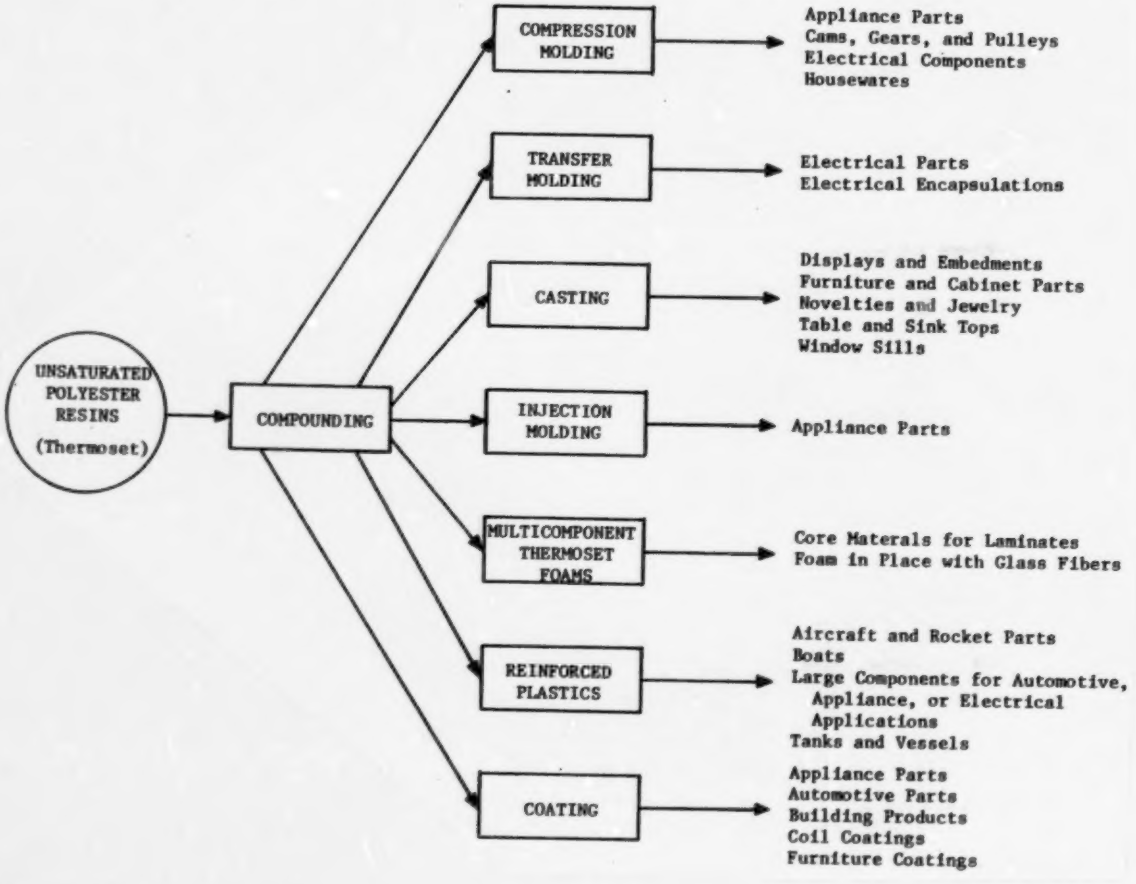

UNSATURATED POLYESTER RESINS (Thermoset)
COMPOUNDING
COMPRESSION MOLDING
Appliance Parts
Cams, Gears, and Pulleys
Electrical Components
Housewares
TRANSFER MOLDING
Electrical Parts
Electrical Encapsulations
CASTING
Displays and Embedments
Furniture and Cabinet Parts
Novelties and Jewelry
Table and Sink Tops
Window Sills
INJECTION MOLDING
Appliance Parts
MULTICOMPONENT THERMOSET FOAMS
Core Materals for Laminates
Foam in Place with Glass Fibers
REINFORCED PLASTICS
Aircraft and Rocket Parts
Boats
Large Components for Automotive, Appliance, or Electrical Applications
Tanks and Vessels
COATING
Appliance Parts
Automotive Parts
Building Products
Coil Coatings
Furniture Coatings

Figure B-1 (continued)

APPENDIX C

WORKER EXPOSURE IN THE PLASTICS AND RESINS PROCESSING INDUSTRY

TABLE C-1. OSHA REGULATIONS FOR THERMOSET COMPONENTS AND CURE REACTION BY-PRODUCTS

TABLE C-2. OSHA REGULATIONS FOR AIRBORNE EMISSIONS (VOLATILES AND PARTICULATES)

TABLE C-3. WORKER SAFETY MEASURES FOR ADDITIVES

TABLE C-1. OSHA REGULATIONS FOR THEMOSET COMPONENTS AND CURE REACTION BY-PRODUCTS

Resin	Components and Cure Reaction By-Products	OSHA Standard	NIOSH (a) or ACGIH (b) Recommendation
Amino	Formaldehyde	3 ppm 8 hr. TWA 5 ppm ceiling	0.5 ppm TWA (a) 1 ppm ceiling
	Hydrogen Cyanide	10 ppm (11 mg/m^3)	5 mg/m^3 10 min ceiling (a)
	Nitrogen Oxides	-----	-----
Epoxy	Epichlorohydrin	5 ppm 8 hr. TWA	2 mg/m^3 TWA (a) 19 mg/m^3 15 min ceiling
	Bisphenol-A (Diglycidyl Ether)	0.5 ppm 8 hr. TWA	-----
Phenolic	Phenol (skin)	5 ppm 8 hr. TWA	10 ppm STEL (b)
	Formaldehyde	3 ppm 8 hr. TWA 5 ppm ceiling	-----
	Acetone	1,000 ppm 8 hr. TWA	750 ppm TWA 1,000 ppm STEL
	Ammonia	50 ppm (35 mg/m^3) 8 hr. TWA	50 ppm 5 min ceiling (a)
	Cresols	5 ppm 8 hr. TWA	None
	Furfural	5 ppm (20 mg/m^3) 8 hr. TWA	2 ppm TLV (b)
	Ketones	-----	-----
	Paraformaldehyde	-----	-----
	Resorcinol		10 ppm 8 hr. TWA (b) 20 ppm STEL
	Styrene	100 ppm 8 hr. TWA 200 ppm ceiling 600 ppm 5 min any 3 hr. period	50 ppm 8 hr. TWA (b)
	Sulfuric Acid	1 mg/m^3 8 hr. TWA	1 mg/m^3 8 hr. TWA (a)
	Toluene	200 ppm 8 hr. TWA 300 ppm 10 min ceiling 500 ppm peak	100 ppm 8 hr. TWA (a) 200 ppm 10 min ceiling

(continued)

TABLE C-1 (continued)

Resin	Components and Cure Reaction By-Products	OSHA Standard	NIOSH (a) or ACGIH (b) Recommendation
	Xylene	100 ppm 8 hr. TWA	100 ppm 8 hr. TWA (a) 200 ppm 10 min ceiling
Polyesters	Maleic Anhydride	0.25 ppm 8 hr. TWA	-----
	Phthalic Anhydride	2 ppm 8 hr. TWA	1 ppm 8 hr. TWA (b) 4 ppm STEL
	Isophthalic Anhydride	-----	-----
	Adipic Acid	-----	-----
	Propylene Glycol	-----	-----
	Stryene	100 ppm 8 hr. TWA 200 ppm ceiling 600 ppm 5 min ceiling in 3 hr. period	50 ppm 8 hr. TWA (b)
	Vinyl Toluene	100 ppm 8 hr. TWA	50 ppm 8 hr. TWA (b)
	Methyl Methacrylate	5 mg/m^3	5 mg/m^3 8 hr. TWA (b) 10 mg/m^3 STEL
Polyurethane	Toluene Diisocyanate	0.02 ppm ceiling	0.005 ppm 8 hr. TWA (a,b) 0.02 ppm 20 min period
	Methylene Bisphenyl Isocyanate	0.02 ppm ceiling	50 ug/m^3 8 hr. TWA (a)

Sources: ACGIH, TLVs, Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes, 1978.

NIOSH/OSHA, Occupational Health Guidelines for Chemical Hazards, 1981.

RTECS Data Base.

"Safety and Health Regulations: Government vs. Plastics Processors, An Assessment," Plastics Technology, December 1979, p. 74.

Sittig, Marshall, Handbook of Toxic and Hazardous Chemicals, 1981.

Standen, A., ed., Kirk-Othmer Encyclopedia of Chemical Technology, 1978-1982 (Vol:pg) 2:467, 17:404-405.

TABLE C-2. OSHA REGULATIONS FOR AIRBORNE EMISSIONS (VOLATILES AND PARTICULATES)

Additive Class	Chemical and/or Decomposition Products	OSHA Regulation	NIOSH (a) or ACGIH (b) Recommendations
Antioxidants	2,6-Di-tert-butyl-4-methyl phenol	No standard	10 mg/m^3 8 hr. TWA (b) 20 mg/m^3 STEL
	Trisnonylphenyl phosphite	No standard	-----
	Dilaurylthiodipropionate	No standard	-----
Blowing Agents	Azodicarbonamide decomposes at 195-200°C		
	N_2 (65%)	No standard	-----
	CO (32%)	50 ppm 8 hr. TWA	35 ppm 8 hr. TWA (a) 200 ppm ceiling
	CO_2 (3%)	5000 ppm 8 hr. TWA	10,000 ppm 8 hr. TWA 30,000 ppm 10 min. ceiling
	NH_3	50 ppm 8 hr. TWA	50 ppm 5 min. ceiling
	Azobisisobutyronitrile decomposes at 105°C		
	N_2	No standard	-----
	Tetramethyl succinonitrile (skin) (residue)	0.5 ppm TWA	2 ppm STEL (b)
	Methylene Chloride	500 ppm TWA 1000 ppm ceiling 2000 ppm 5 min. ceiling	75 ppm 8 hr. TWA (a) 100 ppm TWA (b) 500 ppm STEL
Colorants	Carbon Black	3.5 mg/m^3 TWA	3.5 mg/m^3 8 hr. TWA (a) 0.1 mg/m^3 8 hr. TWA in presence of polycyclic aromatic hydrocarbons 7 mg/m^3 STEL (b)

(continued)

TABLE C-2 (continued)

Additive Class	Chemical and/or Decomposition Products	OSHA Regulation	NIOSH (a) or ACGIH (b) Recommendations
Colorants (Cont.)	Titanium Dioxide	15 mg/m^3 8 hr. TWA (nuisance dust)	10 mg/m^3 8 hr. TWA (total) (b) 5 mg/m^3 8 hr. TWA (respirable) (b) 20 mg/m^3 STEL
	Cadmium Sulfoselenide	0.2 mg/m^3 8 hr. TWA 0.6 mg/m^3 ceiling (as Cd)	40 ug/m^3 8 hr. TWA (a) 200 ug/m^3 15 min. ceiling (a) 0.05 mg/m^3 8 hr. TWA (b) 0.20 mg/m^3 STEL (b)
	Lead Chromate	50 ug/m^3 8 hr. TWA (as Pb) 100 ug/m^3 ceiling (as Cr(VI))	25 ug/m^3 8 hr. TWA (as Cr(VI)) (a) 50 ug/m^3 15 min ceiling (a) (as Cr(VI)) 50 ug/m^3 8 hr. TWA ($PbCrO_4$) (b)
	Phthalocyanines	No standard	-----
	Anthaquinone Red	No standard	-----
	Monoazo Yellow	No standard	-----
Flame Retardants	Antimony Oxide	0.5 mg/m^3 8 hr. TWA	0.5 mg/m^3 8 hr. TWA (a)
	Alumina Trihydrate	5 mg/m^3 (total) 8 hr. TWA	5 mg/m^3 8 hr. TWA (respirable) (b)
	Trixylenyl phosphate	No standard	
	Decabromodiphenyl Oxide	No standard	
	Chlorinated Paraffin Wax	2 mg/m^3 8 hr. TWA as paraffin wax fume	6 mg/m^3 STEL (b)
Heat Stabilisers	Tribasic Lead Sulfate	50 ug/m^3 8 hr. TWA (as Pb)	0.15 mg Pb/m^3 8 hr. TWA (a and b) 0.45 mg/m^3 STEL

(continued)

TABLE C-2 (continued)

Additive Class	Chemical and/or Decomposition Products	OSHA Regulation	NIOSH (a) or ACGIH (b) Recommendations
Heat Stabilizers (Cont.)	Ba/Cd Stearate	0.2 mg Cd/m^3 8 hr. TWA 0.6 mg/m^3 ceiling	40 ug/m^3 8 hr. TWA (a) 200 ug/m^3 5 min. ceiling (a) 0.05 mg/m^3 8 hr. TWA (b) 0.20 mg/m^3 STEL (b)
	Ca/Zn Stearate	No standard	10 mg/m^3 8 hr. TWA Total (as zinc stearate) (b) (nuisance dust)
UV Stabilizers	2-Hydroxy-4-octoxy-benzophenone	No standard	-----
	2-(2'-Hydroxy-5'-methylphenyl) benzotriazole	No standard	-----
	Nickel dibutyldithio carbamate	No standard	15 ug/m^3 8 hr. TWA
Urethane Catalysts	Triethylene diamine	No standard	-----
	Stannous octoate	0.1 mg(as Sn)/m^3 8 hr. TWA	0.1 mg(as Sn)/m^3 8 hr. TWA
Plasticizers	Dioctyl phthalate	No standard	-----
	Diisooctyl phthalate	No standard	-----
	Diisodecyl phthalate	No standard	-----
	Tricresyl phosphate	Ortho - 0.1 mg/m^3 8 hr. TWA 0.3 mg/m^3 No standard for meta and para	-----
	Di-(2-ethylhexyl) phthalate	No standard	-----
Reinforcing Agents	Glass fibers (fused quartz)	$\frac{10\ mg/m^3}{\%\ SiO_2 + 2}$ (respirable quartz)	5 mg/m^3 8 hr. TWA (total)
	Asbestos	0.5 fiber <5 um/cc	$0.1x10^6$ fibers/m^3 <5 um 8 hr. TWA (a) $0.5x10^6$ fibers/m^3 <5 um 15 min. ceiling

(continued)

TABLE C-2 (continued)

Additive Class	Chemical and/or Decomposition Products	OSHA Regulation	NIOSH (a) or ACGIH (b) Recommendations
Reinforcing Agents (Cont.)	Silica (Crystalline)	20 mppcf	10 mg/m^3 8 hr. TWA (b)
		$\frac{10\ mg/m^3}{\%\ SiO_2 + 2}$ (respirable quartz)	50 ug/m^3 8 hr. TWA

Sources: ACGIH, TLV's, Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes, 1982.

Hawley, Gessner, G., The Condensed Chemical Dictionary, 1977.

Kirk-Othmer Encyclopedia of Chemical Technology, 1978-1982, Vol. 10, p. 214; Vol 4, p. 654-7.

Nass, Leonard I., Encyclopedia of PVC, 1977, p. 812.

NIOSH/OSHA, Occupational Health Guidelines for Chemical Hazards, 1981.

Polymer Additives: Guidebook and Directory, 1972, pp. 444, 247.

RTECS Data Base

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TABLE C-3. CONTROL MEASURES FOR ADDITIVES

Additive Class	Chemical	Concern	Recommended Control Measures
Antioxidants	2,6-Di-tert-butyl-4-methyl phenol	Slightly toxic	Poses no undue hazard in handling and use. Normal safety precautions and good housekeeping.
	Trisnonylphenyl phosphite	Inhalation Skin contact	Ventilation Avoid skin and eye contact - rubber gloves and safety glasses Personal hygiene
	Dilauryl thiodipropionate	Low Toxicity	Poses no undue hazard in handling and use. Normal safety precautions and good housekeeping
Blowing Agents	Azodicarbonamide	Nontoxic	Ventilation (for ammonia and carbon monoxide)
	Azobisisobutyronitrile	Toxic residue forms	Exhaust system Product washed with warm water or heated in annealing oven to remove toxic residue
	Methylene Chloride	Toxic Eye irritant Potential carcinogen	Protective clothing - eye protection Personal hygiene Respirators
Colorants	Carbon Black	Irritant Possible carcinogen Absorbs oxygen	Bag filters Avoid eye contact - goggles Personal hygiene Respirators and dust masks Good housekeeping
	Titanium Dioxide	Slight lung fibrosis	Respirators and dust masks
	Cadmium Sulfoselenide	Toxic Carcinogen	Exhaust ventilation and general dilution ventilation Good housekeeping Protective clothing - gloves, goggles, face shields, impervious clothing Personal hygiene Respirators

(continued)

TABLE C-3 (continued)

Additive Class	Chemical	Concern	Recommended Control Measures
Colorants (Cont.)	Lead Chromate	Irritant Toxic Carcinogen	Ventilation Personal protection - clothing, eye protection Personal hygiene Respirators (>50 ug/m^3 (as Pb)) Good housekeeping
	Phthalocyanines		Adequate ventilation
	Anthraquinone Red		Adequate ventilation
	Monazo Yellow		Adequate ventilation
Flame Retardants	Antimony Oxide	Primary skin irritant (antimony "fleas") Toxic Dermatitis Respiratory irritant	Adequate ventilation Protective clothing - barrier creams, gloves, eye protection Personal hygiene Dust masks and respirators
	Alumina Trihydrate		
	Trixylenyl Phosphate	Respiratory irritant Nausea Skin absorption	Avoid skin and eye contact
	Decabromodiphenyl Oxide	No toxicity has been found	
	Chlorinated Paraffin Wax		
Heat Stabilizers	Tribasic Lead Sulfate		Closed conveying systems Dust collection equipment Ventilation Respirators (>50 ug/m^3 (as Pb))
	Ba/Cd Stearate		
	Ca/Zn Stearate		

(continued)

TABLE C-3 (continued)

Additive Class	Chemical	Concern	Recommended Control Measures
UV Stabilizers	2-Hydroxy-4-octoxy-benzophenone		
	2(2'-Hydroxy-5'-methylphenyl) benzotriazole		
	Nickel dibutyldithio carbamate	Toxic Irritant	Adequate ventilation Avoid skin contact Respirators and dust masks
Urethane Catalysts	Triethylene Diamine	Combustible Irritant	Avoid eye and skin contact - clothing, goggles Respirators
	Stannous Octoate	Toxic Irritant	Process enclosure General dilution and local exhaust ventilation Personal protective equipment - gloves, goggles, face shield, impervious clothing Respirators
Plasticizers	Dioctyl phthalate	Irritant	Protective clothing - safety glass, gloves Respirators and gas masks No eating in work area
	Diisooctyl phthalate		Protective clothing - gloves
	Diisodecyl phthalate		Protective clothing - gloves
	Tricresyl phosphate	Nervous system toxicity (polyneuritis) Skin absorption	General ventilation Protective clothing - gloves, barrier creams, eye protection Personal hygiene Respirators
	Di-(2-ethylhexyl)phthalate	Potential Carcinogen	

(continued)

TABLE C-3 (continued)

Additive Class	Chemical	Concern	Recommended Control Measures
Reinforcing Agents	Glass fibers	Irritant	Local exhaust ventilation and collection system Protective clothing - gloves, clothing, eye protection Respirators and dust masks Personal hygiene
	Asbestos	Asbestosis Carcinogen	Dust collection systems Fabric filter bag houses Automatic opening and loading devices Closed systems Protective clothing - coveralls, resin impregnated paper clothing Personal hygiene
	Silica	Silicosis Skin and mucous membrane drying	Local exhaust and general dilution ventilation Process enclosure Dust masks and respirators

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